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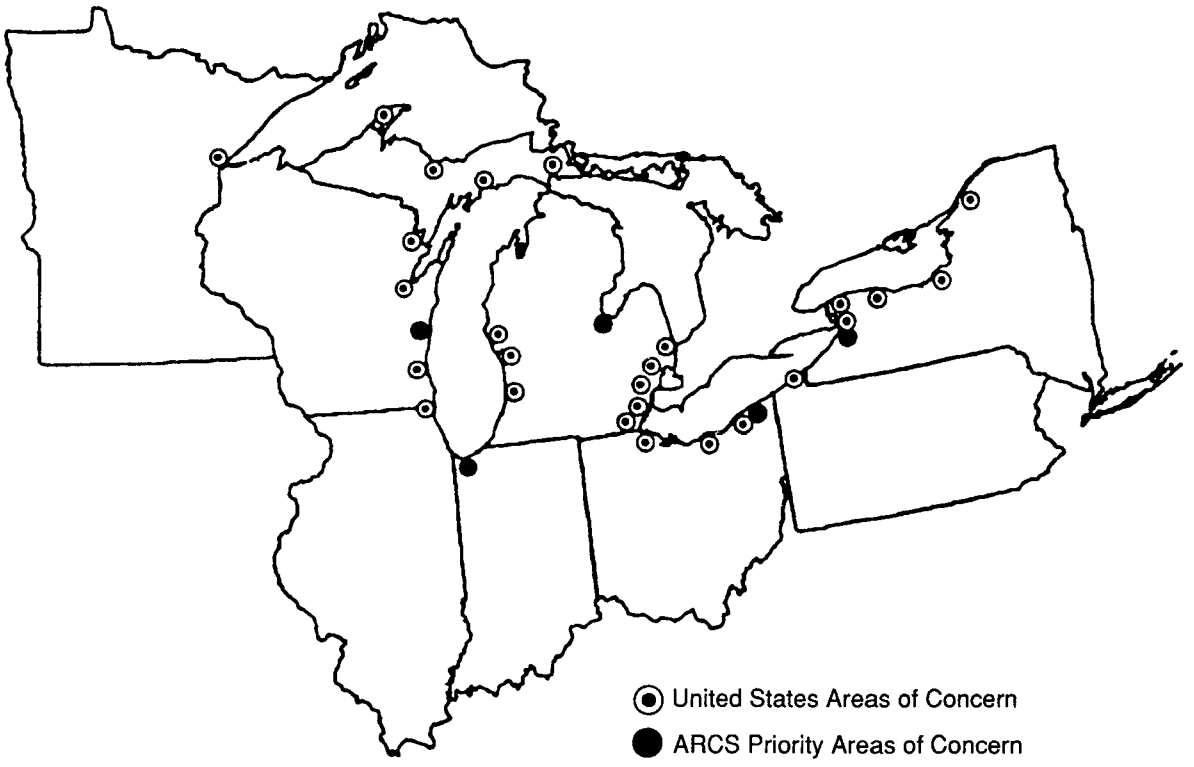
Hazard Ranking of Contaminated Sediments Based on Chemical Analysis, Laboratory Toxicity Tests, and Benthic Community Structure: Method of Prioritizing Sites for Remedial Action



Hazard Ranking of Contaminated Sediments Based on Chemical Analysis, Laboratory Toxicity Tests, and Benthic Community Structure: Method of Prioritizing Sites for Remedial Action

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INTRODUCTION

Contaminated sediments have become a major focus of environmental concern and research, particularly in the Great Lakes (USEPA 1990). The concern is that even with elimination of current and future sources of contamination, those contaminants already present in sediments are a threat to aquatic life and human health. The Assessment and Remediation of Contaminated Sediments (ARCS) program was managed by the Great Lakes National Program Office of the United States Environmental Protection Agency (USEPA) specifically to address contaminated sediment issues in the Great Lakes and to examine new and innovative ways to both assess and treat contaminated sediments (USEPA 1990).

One goal of the ARCS program was to develop a method by which the relative risks associated with contaminated sediment from different sites can be evaluated. A general method of ranking contaminated sediments based upon direct sediment analyses and tests proposed by Kreis (1989) and was used to proportionally scale sediment variables so that they could be compared and combined. The ranking method developed for ARCS was modified and enhanced from the version proposed by Kreis (1989) by incorporating bioavailability, control-adjusted laboratory toxicity tests, and mean tolerance to pollution of the benthic community for the sediments of concern.

The numerical ranking system developed by Kreis (1989) was intended as a guide, to be used in evaluating regulatory and remediation alternatives for contaminated Great Lakes sediments. Kreis (1988) previously showed that the

ranking process can be an effective tool for determining which sites, of a set of contaminated sites, have the highest concentrations of total contaminants and associated parameters. The results of the ranking process can then be used to prioritize sites for remediation; this prioritization is necessary due to the high cost of sediment remediation. As resources and technologies become available, the sediments needing remediation could each be "cleaned-up" in the order of their ranking. The remediation procedure or combination of procedures chosen is site-specific and would depend on ecological, chemical, economic, and engineering considerations.

OVERALL HAZARD RANKING

In this report, we used the process of proportional scaling from 1 to 100 (Kreis 1989) to scale different types of information (i.e., sediment chemistry, laboratory toxicity, and benthic community structure) in a way that they can be evaluated equivalently. As suggested by Kreis (1989), once all the information was on the same scale, the data were combined by averaging (i.e., arithmetic mean) the information from all three categories. The site mean of the proportionally scaled values was then considered to be the best estimate of relative hazard, among sites, of sediment contaminants to aquatic life.

The primary difference between this relative ranking process and the earlier process (Kreis 1989) is that this one incorporates more information, including: 1) adjustment of the bulk sediment chemistry concentrations for estimated

bioavailability and cumulative chronic toxicity through the use of "toxic units" (defined in the next section); 2) incorporating of control-adjusted laboratory toxicity test results; and 3) incorporating of benthic community information, in the form of mean tolerance to pollution per organism for each site.

Ranking Sites Based on Toxicity Estimated from Chemistry Data

In the ranking system developed by Kreis (1989), each chemical or group of chemicals (e.g., metals, dioxins, etc.) analyzed was ranked independently. For each analyte or group of analytes, the measured values or totals, respectively, representing each site under consideration were scaled from 1 to 100, relative to each other (i.e., the minimum measured value became 1, the maximum, 100). The equation used to calculate the ranks for each chemical or group of chemicals was:

$$Rank = 1 + \frac{Site\ value - Minimum\ value}{Maximum\ value - Minimum\ value} \times 99$$

The independent ranks calculated for each chemical or group of chemicals was then combined by averaging (arithmetic mean) for each site, yielding a mean rank for each site based on chemical concentrations. In this ranking process the chemicals analyzed are scaled relative to each other based only on the concentrations present; the process does not scale those chemicals based on the true measure of concern, which is hazard. In addition to analyte concentration,

hazard also includes a toxicity component.

The approach we present for evaluating the hazard associated with chemicals in sediments includes toxicological, ecological, and bioavailability information. In contrast to the earlier method (Kreis 1989), in our approach the "toxic units" (Sprague and Ramsay 1965) for each contaminant measured are calculated. Sprague and Ramsay (1965) defined a toxic unit as the ratio of observed water concentration of a contaminant to the incipient lethal concentration of that contaminant. Our definition of a toxic unit is similar, but based on the USEPA Ambient Water Quality Criteria (AWQC); we define a toxic unit as the ratio of the estimated bioavailable component of the contaminant to the chronic toxicity water quality criteria (e.g. USEPA 1986a) for that contaminant. We estimate contaminant bioavailability by assuming that concentrations of the water-soluble, bioavailable fractions of organic chemicals are controlled by equilibrium partitioning (DiToro et al. 1991), and that acid volatile sulfides control the solubility and bioavailability of metals (DiToro et al. 1990). Our estimates of chronic toxicity are based heavily on the AWQC for chronic toxicity (e.g., USEPA 1986a), which incorporate laboratory-measured chronic toxicity--which indirectly incorporates bioaccumulation and measured bioaccumulation.

In our approach, total potential toxicity is calculated by summing toxic units over all contaminants measured for each site. This total potential toxicity is then ranked among sites using the ranking equation described earlier (Kreis 1989). The result is a relative ranking of the sites under investigation based on the cumulative

knowledge of what is known about the potential bioavailability and toxicity of the contaminants found in the sediments at each site. In our approach the analytes present in sediments are scaled for toxicity and bioavailability and combined (summed). These sums are then ranked.

Toxic units model

To estimate toxicity of a complex mixture of chemicals, we used an additive model based on toxic units. A toxic unit is defined here as the ratio of the estimated concentration of a contaminant in the pore water of a test sediment to an estimate of chronic toxicity of that contaminant in water. The equation for toxic units is:

$$\textit{Toxic unit} = \frac{\hat{C}_{wp}}{C_{wqs}}$$

$\hat{C}_{wp}$ = *Estimated pore-water concentration*
C_{wqs} = *Water quality standard*

The toxic units for the contaminants in a sediment are then summed to produce a total toxicity estimate for that sediment.

Estimated pore-water concentrations

Pore-water concentrations of the contaminants are estimated on the basis of equilibrium partitioning and organic carbon control for organic compounds (DiToro et al. 1991) and AVS and sulfide control for metals (DiToro et al. 1990). The estimated pore-water concentrations are considered estimates of the bioavailable portions of the total concentrations of each contaminant measured in the sediments (i.e., the concentration to which sediment-dwelling organisms would be exposed at equilibrium).

Pore-water concentrations of organic compounds were estimated from the total sediment concentration in two ways: 1). by assuming complete bioavailability of bulk sediment concentrations; and 2). by correcting for organic carbon using equilibrium partitioning (DiToro et al. 1991). The intent of using both methods was to evaluate how well the toxic units model predicted toxicity of sediments as measured by control-adjusted laboratory toxicity tests and mean tolerance to pollution of the benthic community and how the ranking of hazard among sites compared with and without accounting for bioavailability through equilibrium partitioning. In the bulk-sediment approach, organic analytes are considered completely bioavailable; that is, the pore-water concentration was estimated by multiplying the dry weight concentration of each analyte by the dry weight to moisture content ratio of the sediment. In the equilibrium partitioning method, the pore-water concentration for organic contaminants and, hence, the bioavailability, of each analyte is assumed to be controlled by organic carbon content of the

sediment, and is consequently a function of the organic carbon partition coefficient (K_{oc}) of the analyte. We used equilibrium partitioning modeling to estimate the pore-water concentration of each analyte on the basis of the bulk (i.e., dry-weight) sediment concentration, the arithmetic mean log octanol/water partition coefficient (Table 1), and the proportion of organic carbon in the sediment sample associated with that analyte, as follows:

$$\hat{C}_{wp} = \frac{C_s}{K_{oc} P_{oc}}$$

Where:

C_{wp} = *Pore-water analyte concentration*;

C_s = *Bulk-sediment analyte concentration*;

$Log(K_{oc})$ = 0.983 *x* $Log(K_{ow})$ + 0.00028 (*Ditoro et al.* 1991)

K_{ow} = *Octanol/water partition coefficient*;

K_{oc} = *Sediment organic carbon partition coefficient*; *and*

P_{oc} = *Proportion of organic carbon in the sediment*

The main source of K_{ow} values was USEPA (1987a); however, this document did not contain K_{ow} values for all analytes. For those organic analytes lacking a K_{ow}, the following substitutions were made: Chlorodioxins and chlorodibenzofurans lacking K_{ow} values were assumed to have the same K_{ow} as a chlorodioxin with the same number of chlorines for which a value was available; for endrin ketone (a

polar metabolite of endrin) the K_{ow} of endrin aldehyde (another polar metabolite) was substituted; and for cis- and trans-chlordane, the K_{ow} for technical chlordane, a complex mixture containing these and other constituents, was used.

Analogous to the methods used for organic contaminants, pore-water concentrations of metals were also estimated from the bulk sediment concentration in two ways: 1). by assuming complete bioavailability of bulk sediment concentrations; and 2). by correcting for AVS by using the concentrations of metals simultaneously extracted with AVS (i.e., simultaneously extracted metals--SEMs) adjusted for AVS (DiToro 1990). In both methods, the estimated pore-water concentration was the estimated bioavailable concentration (entire sediment concentrations in the first method) multiplied by the dry weight to moisture content ratio of the sediment. In the first method, the full concentration of each metal present in the sediment is considered bioavailable. In the second, only those metals extractable with a weak acid (1-N HCl) and adjusted for the potential sulfide salts that could be formed by the extracted metals are considered bioavailable. As described for organic contaminants and organic carbon, the intent of using these two methods was to evaluate how well the toxic units model predicted the toxicity of sediments based on control-adjusted laboratory toxicity tests and mean tolerance to pollution of the benthic community and how the ranking of hazard among sites compared with and without AVS limitation.

The AVS model is based on the assumption that under the reducing conditions present within sediments, sulfides control the pore-water concentrations and,

hence, bioavailability of divalent metals. The sulfide salts of the metals are relatively insoluble; the formation of these salts thereby renders the divalent metals unavailable. AVS modeling of pore-water concentrations therefore adjusts the maximum potential pore-water concentrations of metals downward based on the amount of AVS present.

In the ARCS sediments, the total molar concentrations metals simultaneously extracted with AVS frequently exceeded the molar sulfide concentration. Consequently, it was necessary to apportion the sulfide among the divalent metals and arsenic present. We allocated AVS to metals and arsenic based on the solubility product constants, K_{sp}, of their sulfide salts (Weast et al. 1988). Accordingly, AVS was allotted to metals in the following order: mercury, silver, copper, cadmium, lead, zinc, nickel, arsenic, iron, manganese, and chromium (i.e., mercuric sulfide is the least soluble and chromium sulfide the most soluble sulfide). An equimolar amount of AVS was allotted to each metal in the order of their K_{sp} until either all AVS was allotted or all metals were sulfide-bound. For selenium, which is not controlled by AVS, we used the bulk-sediment concentration and the sediment quality standard proposed by Lemly et al. (1993).

Water quality standards

Relative potential toxicity was estimated from chronic toxicity information for each analyte (Table 2), the primary source of which was the series of AWQC documents. The calculation of chronic toxicity AWQC incorporates information

both on chronic toxicity of a contaminant to various forms of aquatic life and the bioconcentration factor of the contaminant in aquatic ecosystems. Thus, this estimate of chronic toxicity is also more indicative of the severity of long-term exposure to a contaminant for aquatic organisms than would be a direct measure of toxicity. In addition, many of the so-called "short-term" tests performed under the ARCS Program, and against which we compare the results of the toxic units model, are in fact longer in duration than 96 h and include sublethal endpoints such as growth and behavior. Hence, they are more appropriately compared to the chronic criteria.

For those analytes without AWQC, chronic toxicity values were obtained from other sources (Table 2). We used the chronic toxicity values of the Michigan Department of Natural Resources 1993 Water Quality Standards (unpublished data) for the dichlorobenzenes, naphthalene, silver, and tributyltin. For dibenzofuran, bis(2-ethylhexyl)phthalate, and dimethyl phthalate, we estimated a value by proportionally adjusting the Michigan DNR chronic toxicity standard for 1,2-dichlorobenzene on the basis of the ratio of 1,2-dichlorobenzene toxicity to that of the other compounds (LeBlanc 1980). For the chlorodioxins, chlorodibenzofurans, and polychorinated biphenyls (PCBs), we estimated a value by proportionally adjusting the Aroclor® 1254 AWQC (USEPA 1980a) in two steps: First, we determined the ratio of the aryl hydrocarbon hydroxylase (AHH) activity of Aroclor® 1254 to that of TCDD and the ratio of the AHH activity of Aroclor® 1254 to that of each compound (Smith et al. 1990). For some isomers and congeners, the ratio

of AHH activity of Aroclor® 1254 to that of TEF of each compound (Safe 1990) was used. We then used the ratio of these two values as a proportionation factor to adjusted Aroclor® 1254 values. For most polycyclic aromatic hydrocarbons (PAHs), a chronic toxicity estimate was back-calculated using equilibrium partitioning from a sediment threshold (USEPA 1985a) by assuming 4% organic carbon (the value used to generate the threshold concentrations) and the K_{oc} values used in the model presented here; for benzo(g,h,i)perylene and fluoranthene, chronic toxicity was estimate from the ratio of the toxicity of each to the toxicity of benzo(a)pyrene multiplied by the estimated water quality standard for benzo(a)pyrene (Newsted and Giesy 1987); and dibenzofuran and naphthalene were noted previously.

For the following groups of analytes, lacking more information, the chronic toxicity estimates used in the model were defined by the AWQC for the parent compound or formulation of the analyte: For cis- and trans-chlordane, we used the technical chlordane AWQC (USEPA 1980c); for DDD, DDE, and DDT, the p,p'-DDT AWQC (USEPA 1980d); for α- and β-endosulfan, and endosulfan sulfate, the endosulfan AWQC (USEPA 1980e); for endrin, endrin aldehyde, and endrin ketone, the endrin AWQC (USEPA 1980f); and for heptachlor and heptachlor epoxide, the heptachlor AWQC (USEPA 1980g). For selenium we used the sediment quality value recommended by Lemly et al. (1993), and, consequently, no pore-water estimate was necessary. For analytes with water quality standards that are dictated by hardness (i.e., cadmium, chromium, lead, and zinc), the hardness

values used in the calculations for individual sediments were those measured in the 14-d flow-through sediment toxicity test with Chironomous riparius, one of the ARCS laboratory toxicity tests, for that sediment (Nelson et al. 1993).

Lack of available information precluded the use of several of the compounds measured in the example data set in the ranking process. These included: the α, β, and δ isomers of hexachlorocyclohexane; dimethyl butyl phthalate; di-n-octalphthalate; 2-methyl naphthalene; 4-methyl naphthalene; and benzo(b)flouranthene, for which toxicity information was lacking; and monobutyl- and dibutyl-tin, for which K_{ow} values were not available.

Other information

The potential toxicity of ammonia in the ARCS sediments prompted the inclusion of the unionized ammonia levels associated with the 14-d Chironomous riparius sediment toxicity test for each sediment (Nelson et al 1993). The toxicity of ammonia and, hence, the AWQC for ammonia (USEPA 1985b) are pH-dependent. Consequently, we used the pH values measured during the same toxicity tests to estimate the AWQC for unionized ammonia.

Ranking Sites Based on Toxicity as Measured by Laboratory Toxicity Tests

When the results of multiple laboratory sediment toxicity tests and multiple endpoints measured within some tests are to be used together, the data from each toxicity test and multiple endpoints measured within some tests had to be scaled

equivalently (analogous to the toxic units scaling performed on the suite of chemistry measures). This was accomplished by normalizing the measured response associated with an endpoint to the control sediment response for that endpoint:

$$\textit{Control-adjusted laboratory toxicity response} = 1 - \frac{\textit{Endpoint value for test sediment}}{\textit{Endpoint value for control sediment}}$$

Adjusting a test response to its control scales that measure as a proportion of its control, and it also adjusts the responses for the conditions present at the time of the test. The latter accounts for variation attributable to the tests being run at different times, in different locations, by different investigators, or combinations of these factors. So that the control-adjust laboratory toxicity response ordered the sites in the same fashion with respect to toxicity as the toxic units model (i.e., lowest value = least toxic and highest value = most toxic), the ratio of the endpoint value for the test sediment:endpoint value for the control sediment was subtracted from one, as shown in the last equation. The estimates of hazard--the control-adjusted laboratory toxicity responses for each endpoint--were then averaged (i.e., arithmetic mean) over all measured endpoints for a site to estimate the mean hazard for each site based on laboratory toxicity. This mean estimated hazard was then ranked among sites.

In some tests (e.g., 48-hour Daphnia magna survival--Table 3), multiple concentrations of the test medium were used to estimate LC50s, which yield little information compared to the actual response at individual concentrations, and which are not scalable to the control. For such tests, a response was first multiplied by the proportion of the full concentration of the medium at which the test was run (i.e., 50% elutriate response was multiplied by 0.5) before the proportional laboratory toxicity response was calculated. This "proportionation factor" gave the observed response for each concentration an equivalency to 100% (i.e., the concentration at which the other tests were run) and enabled scaling of the responses relative to controls.

Ranking Sites Based on Toxicity as Measured by Benthic Community Structure

As we described for laboratory toxicity tests, when different measures of benthic community structure and well-being are measured, they must be uniformly scaled for evaluation. The measure we used was Lenat's (1993) biotic index (i.e. mean tolerance-to-pollution per organism). Lenat (1993) presents a extensive list of tolerance to pollution values for all the organisms considered in his estimates of mean tolerance per organism. The mean tolerance is calculated by first assigning each species a relative tolerance value to pollution; the set of tolerance to pollution values for each species presented by Lenat (1993) was based on correlations between water quality and abundance data for each species. Once the tolerance value for each species is obtained, the mean tolerance (T) is calculated by

summing the product of the abundance (N_i) and tolerance value for each species at a site (T_i) and then dividing that total by the total number of organisms at a site:

$$T = \frac{\sum_i T_i N_i}{\sum_i N_i}$$

Calculating the mean tolerance to pollution of the benthic community assures that the presence of less tolerant orders influences the ranking of a site (i.e., the site is considered less toxic). Here, it is this mean tolerance to pollution per organism at a site that is ranked among sites. Because Lenat's values were derived for flowing waters in the southeast, tolerance values for some taxa had to be obtained from other sources. Table 4 gives the list of organisms observed in the ARCS sediments, their associated tolerance values, and the source of the value; a few of the tolerance values had to be obtained from another source.

Final Ranking

The rankings that result from the different types of information discussed (i.e. chemistry, laboratory toxicity tests, and benthic community structure) can be combined to produce a final ranking for each site. At this point each type of information has been scaled from 1 to 100. The estimate of relative hazard for the sites under investigation, based on all three types of information, is the arithmetic

mean of the three ranks.

Objectives

In this report, we focus on two main aspects of the just mentioned ranking procedure. The first goal of this report was to evaluate the effectiveness of the toxic units approach at predicting biological endpoints (i.e., laboratory toxicity and benthic community structure). The second goal was to evaluate how site ranking changed as the level of information collected at a site declined.

MATERIALS AND METHODS

Sediment Sampling Locations

Sediment samples were collected at 19 different sites for the ARCS program (Ingersoll et al. 1993). Samples were obtained from the lower reaches of two rivers and one harbor complex: in the Buffalo River, samples from five sites were collected in October, 1989; in the Saginaw River, three sites were sampled in December, 1989, and seven were sampled in June, 1990 (only one of which had been sampled in December); and four Indiana Harbor sites were sampled in August, 1989.

Sampling and Biological Measures

Grab samples of sediment were collected with a 23- x 23-cm Ponar sampler and brought into the laboratory for analysis. At each site, one sample was

collected for chemical analysis and laboratory toxicity tests and five samples were collected for benthic community analyses. Those samples designated for both chemical analysis and laboratory toxicity testing were split into two portions; one portion of each sample was analyzed for contaminants and the other portion was used in laboratory toxicity tests. Those samples designated for benthic community analysis were sieved with a 500-um screen and organisms were identified to the lowest possible taxonomic level. Table 3 gives a list of laboratory toxicity tests carried out on the set of sediment samples modeled in this paper and the endpoints measured. Table 4 gives a list of the taxa observed in the set of sediment samples modeled in this paper, the tolerance value used for each taxon, and the reference from which the tolerance value was obtained. Further details of sample collection, handling, preparation, and testing are presented elsewhere (Ingersoll et al. 1993).

Chemical Analyses

A variety of methods were used to measure contaminant concentrations in the ARCS sediment samples. A subsample of the analytical portion of each sediment was freeze-dried to gravimetrically estimate percent solids. A second subsample was analyzed with a carbon determinator to estimate total organic carbon. A third subsample was used to estimate acid volatile sulfides (AVS) by leaching with 1-N HCL; simultaneously extracted metals (SEM) were determined by analyzing the resulting HCL solutions by atomic absorption spectroscopy. A fourth subsample was completely digested with acids and analyzed for total metals by atomic

absorption. Crustal elements were estimated from a fifth, freeze-dried subsample of sediment analyzed by x-ray fluorescence. Methylmercury was estimated from a sixth subsample of sediment digested in potassium hydroxide and analyzed by atomic fluorescence. Organotins were quantified by gas chromatography from a seventh subsample after extraction with 0.2% tropolone. Organic chemical residues (i.e., PAHs, PCBs, chlorinated pesticides, PCDDs, and PCDFs) were extracted with methylene chloride (all but PCDDs and PCDFs) or benzene (PCDDs and PCDFs) from subsamples eight and nine, respectively, and analyzed by gas chromatography and mass spectrometry. Further details of these chemical analyses can be found elsewhere (Ingersoll et al. 1993).

Detection Limits

To complete this study, we had to account for differences in analytical sensitivity among samples by defining for each analyte one censoring level to be applied to all samples. We needed to ensure that an analyte measured with low sensitivity (i.e., high detection limit) did not control the toxic units estimate for any sample only because of that analyte's high detection limit. To eliminate this possibility, we censored at the highest detection limit among samples for each analyte; i.e., any concentrations, detected or not, that were at or below this censoring level were assumed to be zero. The censoring process we used for the ARCS chemistry data was the most appropriate alternative because the data had been collected prior to the development of the model; preliminary analyses revealed

that many of the toxic units values derived from the ARCS sediment chemistry data were defined by the analytical sensitivity (i.e., detection limits) of the methods used to measure the various analytes. The detection limits for one set of Saginaw River sediments were so high that they completely dominated the hazard assessment. Consequently, data from the seven Saginaw River sites sampled in June of 1990 were not included in the analyses presented here; our analyses are based on samples from the other 12 ARCS sites, all of which had much lower and more consistent detection limits.

Toxic Units Model Evaluation

Model predictions were analyzed by simple regression and correlation. We assessed the ability of various forms of the toxic units model (e.g., with and without certain variables) to predict mean control-adjusted laboratory toxicity and/or mean tolerance to pollution of the benthic community on the basis of regression results, which were evaluated in terms of R^2- and P- values. A model was considered a better predictor of toxicity than other models if it accounted for a larger percentage of the variability observed in the measured response (i.e., mean control-adjusted laboratory toxicity or mean tolerance to pollution of the benthic community).

Ranking Evaluation

In the ARCS program, there were three categories of collection sites for sediments: Priority Master Stations, Master Stations, and Reconnaissance Stations. The difference between the categories of stations was in the number of parameters measured. At Priority Master Stations, all chemistry (Table 2), laboratory toxicity (Table 3), and benthic community (Table 4) measurements were made. At Master Stations, all chemistry, a shortened list of laboratory toxicity ('*' tests in Table 3), and all benthic community measurements were made. At Reconnaissance Stations, only a short list of contaminants (i.e. cadmium, chromium, copper, iron, nickel, lead, zinc, unionized ammonia, and total Aroclor^{R}s) and Microtox^{R} were measured. The intent of this gradient of information collected at each site was designed to determine how much information was actually needed to effectively evaluate the relative contaminant hazard among a group of sites.

As directed under the ARCS program, we evaluated the effect of different amounts of information on the resultant final ranking of the sites. We compared and contrasted the final ranking among sites when Priority Master Station indicators were used as opposed to when: 1). Master Station indicators were used; 2). Reconnaissance indicators were used; and, 3). only the contaminants considered bioaccumulative were used in the toxic units model with the full bulk sediment concentration of each contaminant considered bioavailable. The latter question was added on our part based upon our review of the draft Great Lakes Water Quality Initiative (USEPA 1993) (Table 5). We wanted to know the extent

to which the relative ranking of sites changed when the set of information used in the process was reduced. In other words, what is the minimal, most cost-effective suite of measurements required to accurately rank the sites? The assessment of the extent to which the ranking changed was measured by the change in the amount of variation explained by the full model rankings when reduced sets of data were used to rank the sites (i.e., change in R^2). The fact that comparisons were limited to pairs of ranks allowed us to use simple correlation analysis. We used the Statistical Analysis System (SAS Institute 1990) for all data management, computations, and statistical analyses.

RESULTS

Toxic Units Model

Laboratory toxicity

The best predictor of laboratory toxicity was the full model of bioavailable contaminants, which included both organic carbon control for organic contaminants and AVS control for inorganics (Figure 1). This model accounted for more than 89% of the variability present in mean laboratory toxicity. When bulk contaminant concentrations were substituted for bioavailable fractions, the model accounted for only 68% of the variability (Figure 2). Among the ARCS sites, predicted toxicity of Indiana Harbor site 3 was the most greatly affected when equilibrium partitioning and AVS were excluded from the model; toxicity at this site was accurately estimated by the full model, but greatly underestimated by the bulk

chemistry model (cf. Figures 1 and 2).

Tables 6-8 give the list of individual contaminants that were estimated to be present at at least one toxic unit at one or more sites within an area of concern (e.g., Saginaw River), based on bioavailability chronic toxicity. These lists are shorter than the full list of contaminants measured because not all PCB mixtures, dibenzodioxins, dibenzofurans, etc. were present at toxic concentrations at all sites. The contaminants that contributed the most to the toxic units estimate for a sediment, including iron and ammonia, varied among sites; no single contaminant dominated at all sites (Tables 6-8). In general, only a few contaminants accounted for the greatest percentage of estimated toxicity at each site. For example, endosulfan, endrin, methylmercury, and iron contributed most in the Buffalo River; chromium, dieldrin, endosulfan, endrin, heptachlor, iron, methylmercury, PCBs, and tributyl tin the most in Indiana Harbor; and chlordane, heptachlor, iron, and PCBs the most in the Saginaw River.

The full model indicated that unionized ammonia, chromium, and iron were present at potentially toxic concentrations and accounted for much observed variability at most sites (Tables 6-8). Although it probably influenced many laboratory toxicity test results, unionized ammonia alone did not explain all the toxic effects of the sediments observed in the laboratory; alone it accounted for more than 60% of the variability (Figure 3), substantially less than the full model. The relative toxicity of Saginaw River site 6 was much higher than predicted when ammonia alone was used in the model (cf. Figures 1 and 3). Although iron is only

toxic at relatively high concentrations--1 mg/l (USEPA 1976)--it was also important in the prediction of laboratory toxicity from sediment chemistry. Without iron, the toxic units model (including ammonia) accounted for just over 52% of the variability of the laboratory toxicity test (Figure 4) as compared to 89% with both iron and ammonia included (Figure 1). Without iron, the site with the highest relative toxicity (i.e., Indiana Harbor site 7) was predicted to have about half its measured toxicity (cf. Figures 1 and 4). And finally, replacing the bioavailable fractions with whole-sediment concentrations of those contaminants that are considered Bioaccumulative Contaminants of Concern by USEPA (1993--Table 5), and assuming them to be completely bioavailable, also reduced the model's ability to predict laboratory toxicity. Using only the bioaccumulatives in this fashion, the model accounted for less than 70% of the variability in the laboratory toxicity tests (Figure 5).

Benthic community structure

As described for laboratory toxicity, the best predictor of the mean tolerance value for the benthic community was the full model of bioavailable contaminants, which included both equilibrium partitioning for organics and AVS for metals . This model accounted for 40% of the variability present in the mean tolerance value (Figure 6). When bulk contaminant concentrations were substituted for bioavailable fractions, the model accounted for only 34% of the variability (Figure 7). If only contaminants considered Bioaccumulative Contaminants of Concern by

USEPA (Table 5) are used in the toxic units model, the model accounted for 40% of the variability in the mean tolerance value for the benthic community (Figure 8).

The variability of the mean tolerance value of the benthic community had a different set of relationships with ammonia and iron than did the laboratory toxicity results. In contrast to what was observed for the laboratory toxicity tests, unionized ammonia did not explain a significant amount of the variability in the mean tolerance value of the benthic organisms ($\underline{R}^2 = 0.04$, $\underline{P} = 0.56$). Moreover, without iron, the full model no longer accounted for a significant percentage of the variability in the tolerance value ($\underline{R}^2 = 0.11$, $\underline{P} = 0.31$); for laboratory toxicity tests, the level of significance declined but the full model could still predict the response without iron (Figure 4). In fact, when iron is the only contaminant considered, the model accounted for 40% of the variability in benthic community structure, as it did when all contaminants were considered (Figure 9).

Two other important observations must be noted. First, when only the taxonomic order of each organism, instead of the lowest level of taxonomic identification possible (i.e. mostly genera and species), were used to calculate the mean tolerance value for the benthic community, there were no significant relationships with toxic units in any form. Second, even though we can predict laboratory toxicity and benthic community mean tolerance using the toxic units model, there was no correlation between laboratory toxicity and benthic community mean tolerance ($\underline{R}^2 = 0.21$, $\underline{P} = 0.13$).

Final Rankings

The shortened list of laboratory toxicity indicators (i.e., from Priority Master Station to Master Station indicators), in general, produced the same results as the full set of data (R^2 = 0.99, P = 0.0001; Figure 10). Further exclusion of laboratory toxicity (except Microtox^R) and benthic community data, and using only the short list of sediment contaminant measures (i.e., reducing the Priority Master Stations to Reconnaissance stations) resulted in both increases and decreases in relative toxicity estimates within the set of sites (R^2 = 0.75, P =0.0003; Figure 11). Eight sites, as opposed to only five for the Priority Master Station indicators, had relative toxicity rankings greater than 40 when only Reconnaissance data were used. Also, some sites switched position relative to other sites; for example, Saginaw River site 3 was least toxic with only the Reconnaissance indicators whereas it was sixth most toxic based on all Priority Master Station data.

Using only the data on bioaccumulative contaminants (i.e., ignoring laboratory toxicity and benthic community measures) and assuming the complete bioavailability of all bioaccumulative contaminants (by use of measured bulk sediment concentrations found in the sediment) produced the most dramatic change in relative toxicity of the sites (R^2 = 0.75, P = 0.0003; Figure 12). Relative to the most toxic site (i.e., Indiana Harbor site 7), the estimated toxicity of all other sites decreased greatly. All but three sites that had relative hazard values between 40 and 60 in the case of Priority Master Station data (including Indiana Harbor site 3) had relative toxicities less than 12 when only bioaccumulatives were

used. As a final note, even though we tried different measures to rank the relative toxicity of sites, Indiana Harbor site 7 was always the most toxic, followed by Saginaw River site 6.

DISCUSSION AND CONCLUSIONS

Effectiveness of the Toxic Units Model

Laboratory toxicity

Based upon our comparisons of different model permutations, the best estimate of toxicity was produced by the model that incorporated bioavailability calculations and included the fullest list of potential contaminants. Without estimates of bioavailability, comparisons with toxicity data inherently assumed that all contaminants are completely bioavailable, which greatly reduced model fit. Conversely, without consideration of the toxic effects of contaminants that are only toxic at relatively high concentrations, such as iron, it is inherently assumed that such contaminants are completely nontoxic. The chronic AWQC for iron, for example, is 1 mg/L (USEPA 1976); nevertheless, when iron was excluded the estimated toxicity was also less effective than the full model at predicting observed laboratory effects. Collectively, these findings corroborate previous studies reporting that sediment toxicity, as defined by short-term tests such as those incorporated in the ARCS program, is mediated by pore-water concentrations (Hamelink et al. 1971, Ditoro et al. 1991), and that this toxicity is additive (Safe 1990).

One possible reason for a lack of concordance between the bioaccumulatives and toxicity test results may lie with the PCB component of the ARCS chemistry data set, which is inherently weak. Analyses based on Aroclor® mixtures, as performed for the ARCS program, may not accurately represent the distribution or abundance of toxic PCB congeners in weathered environmental mixtures (Tillitt et al. 1992). Consequently, the TEF approach we used to estimate the toxicity of the PCBs in ARCS sediments, which was based on the dioxin equivalency of unweathered mixtures, may not have been accurate. Better estimates would be obtained through instrumental analyses of individual AHH-active congeners (Kuehl et al. 1991) or, for reconnaissance activities such as those conducted under the ARCS program, through the use of biologically based measurements of dioxin-like activity, as measured by the H4IIE in vitro assay (Tillitt et al. 1991).

Kinetic factors may also greatly affect the sensitivity of sediment toxicity tests to bioaccumulative contaminants. Implicit in the comparison of toxicity test results with equilibrium-based toxic units estimates is the assumption that the equilibrium (or, at least, steady-state) conditions of the site from which the sediment was collected are re-established at the time of the test. No measure of the degree to which this assumption was satisfied was included in the ARCS data set, however, and the rates of such processes may be relatively slow. For this and other reasons, the uptake of sediment-bound, hydrophobic contaminants such as PCBs and dioxins is also slow (Pruell et al. 1993). Moreover, delayed mortality may occur (Mehrle et al. 1988). Collectively, these kinetic factors would tend to make

short-term tests less responsive to contaminants controlled by partitioning and other relatively slow processes than to others. Nevertheless, our modeling results indicate a contribution by PCBs and other hydrophobic contaminants to laboratory-measured toxicity.

Many of the environmental chemistry variables measured in the ARCS sediments were highly intercorrelated, as were the toxicity test results. Such intercorrelation impedes the assessment of causality. This was particularly true for assessing the effects of iron in sediments. Because iron is soluble only in the absence of oxygen (Drever 1982), it could be argued that toxicity attributable to iron is actually caused by a lack of oxygen. In the ARCS study, however, and contrary to our original suspicions, toxicity attributable to the high concentrations of iron in many sediments appeared to be more than just an artifact or surrogate measure of low dissolved oxygen concentrations. Most of the laboratory toxicity tests were performed with reconstituted water, and the dissolved oxygen levels of waters overlying the test sediments were monitored regularly and found to be acceptable in most tests (Nelson et al. 1993). Thus, the improved relationship between laboratory toxicity and toxic units estimates with the inclusion of iron seemed to be directly related to the actual toxicity of the iron which, at the high concentrations present in some ARCS sediments (Tables 6-8), is not surprising.

Although ammonia was present at potentially toxic concentrations at most sites, the contribution to total toxicity of ammonia in the toxic units model was assessed on the basis of unionized ammonia concentrations and pH measured

regularly during the conduct of laboratory toxicity tests. In these tests, the overlying water was reconstituted water and not ambient water. We are not sure how accurately the measurements of ammonia and pH incorporated into the toxic units model represent the ammonia actually present in the natural system prior to sediment collection. To make the estimates of toxicity attributable to ammonia representative of the natural system, the ammonia and pH concentrations in the water overlying the sediment within the natural system should be measured. The same is true for dissolved oxygen, which should also be measured under ambient conditions. Despite the presence of ammonia at potentially toxic levels and its potential to influence the results of the laboratory toxicity tests, ammonia alone was not able to effectively predict the toxicity of the sediments, as noted earlier.

Our findings support the hypothesis that benthic toxicity, as measured by short-term toxicity tests, is mediated by pore-water contaminant concentrations, as has been suggested by others for some time (e.g., Hamelink et al. 1971; DiToro et al. 1990, DiToro et al. 1991). Ecosystem risk, however, has much broader implications, especially for bioaccumulative contaminants, where trophic transfers predominate. With our findings, we have shown that the short-term laboratory toxicity tests are sensitive to iron and ammonia, responses to which may mask the effects of slow-acting, bioaccumulative contaminants. The short-term laboratory toxicity tests, by themselves, appear to reflect toxicity of the sediments in the immediate vicinity from which they are collected, but not necessarily the ecosystem risk represented by the transfer of the contaminants they contain

through the food chain.

Benthic community structure

In the ARCS data, the benthic community structure of contaminated sediments was related to the toxicity of the contaminants present as defined by the toxic units approach. As the estimated toxic units of a sediment increased the mean tolerance to pollution of the benthos community increased. Like the relationship between toxic units and laboratory toxicity test results, the strength of the relationship between toxic units estimates and mean tolerance to pollution declined when, instead of estimated bioavailable concentrations, bulk sediment concentrations of contaminants were used in the toxic units estimates. Unlike the work with laboratory toxicity and toxic units, bioavailable iron toxic units alone had as strong a relationship with mean tolerance to pollution as any other toxic units estimates.

The differences in the observed strength of the relationships among sediment community tolerance, laboratory toxicity test results, and toxic units estimates seems to be an indicator of an information short fall. The much stronger relationship observed between laboratory toxicity and toxic units than between sediment community tolerance and toxic units, seems to indicate an information short fall related to sediment community identification. The observed increased strength of the relationship between toxic units and benthic community tolerance with a finer scale of resolution in taxa identification is an indicator of one possible

way to improve the strength of the relationship. In the ARCS data, the greatest percentage of organisms fell into the category of unidentifiable Tubificidae (i.e. family level identification) (Canfield et al. 1993). From Lenat's (1993) tolerance values, it is apparent that there is a wide range of tolerances among Tubificidae species. It is possible that a finer level of identification (i.e. genera and/or species) would have strengthened the relationship between toxic units estimates and benthic community tolerance.

Another possible contributing factor to the differences in the strength of the relationships among sediment community tolerance, laboratory toxicity test results, and toxic units estimates is that the sediment community tolerance measures a different aspect of contamination than the other two measures. The much stronger relationship between laboratory toxicity and toxic units than between sediment community tolerance and toxic units may be that the sediment community tolerance is more of a long-term measure of effect than the other two measures. This is speculation but it requires further evaluation before it can either be accepted or reject as a cause.

Overall, our results are an indication that the toxic units model is an effective tool for understanding benthic community structure in relationship to complex contaminant mixtures, and that Lenat's (1993) biotic index is a good measure of the effects of pollution, in general, on benthic community structure.

Data quality

Important in the application of a toxic units approach is the consistency and quality of the data. To make accurate environmental-chemistry based comparisons of sediment samples, based on environmental chemistry, the concentrations of any given analyte must be measured with the same sensitivity among the samples to be compared; the censoring level (i.e., detection limit) for any given analyte must be consistent (preferably constant) among samples. If this is not the situation, differences among samples or sites may be controlled by analytical sensitivity rather than true differences among the samples (e.g., two identical samples may appear different if represented by differing detection limit values) which necessitated our elimination of most of the Saginaw River ARCS data from consideration. The best way to avoid the influence of detection limits on toxic units estimates is to define a minimum level of sensitivity for each analyte (i.e., a performance-based criterion). Moreover, this minimum level of acceptable sensitivity should be determined by the level of concern for the analyte. Defining a minimum level of sensitivity for contaminant measurements is only the first step in addressing the problem of detection limits associated with contaminant measurements, the second being how to treat those censored values that inevitably occur. The most environmentally conservative approach would use all values, including censored values in the toxic units model. Because of the expense associated with remediation, the high toxic units estimated using this approach would encourage consistently high sensitivity.

Potential for model enhancements

The methods we used to estimate the bioavailable portions of measured contaminants assume solid-phase control by organic carbon for organic compounds and sulfide for metals and arsenic (DiToro et al. 1990, DiToro et al. 1991). We made no attempt to account for other mechanisms, such as sorption or complexation by other organic or inorganic ligands that might be present in the pore waters. We also assumed complete insolubility of sulfides, an obvious over simplification. Consequently, the models do not predict toxicity of all contaminants at all times (Ankley et al. 1993); nevertheless, they represent the current best estimate of the potential toxicity of sediment contaminants. The toxic units approach incorporated into the model is also versatile; as better methods for estimating the bioavailability of sediment contaminants are developed and water quality standards are revised, such refinements can be incorporated into the modeling process.

It is important to note that if chronic toxicity standards for sediment quality were available, they and actual measured sediment concentrations would be used in the toxic units model instead of AWQC and estimates of pore-water concentrations, respectively. In fact, the proposed Sediment Quality Thresholds for organic chemicals (USEPA 1985a) are founded on estimated pore-water concentrations, equilibrium partitioning, and the AWQC. In the absence of published sediment criteria for all contaminants, however, AWQC and estimation of the pore-water concentration of individual analytes remains the best available

method for estimating toxic units.

The toxic units approach assumes that each contaminant is independent of all other contaminants--i.e., effects are strictly additive. The model does not account for synergistic or antagonist interactions that may occur among contaminants in complex mixtures, even though such interactions are well documented (e.g. Warren 1971, de March 1988, Parrott and Sprague 1993, Schmitt et al. 1993). As information becomes available on the nature of the contradictions to this assumption, quantifiable interactions can be incorporated into the model, along with improvements in the bioavailability estimates. As noted earlier, the model also presently assumes that the bioavailability of divalent metals and arsenic is controlled by AVS. Future model improvements should also include incorporation of other inorganic and organic ligands, perhaps through speciation modeling, to estimate the pore-water concentrations of the divalent ions.

Yet another assumption inherent in our approach is that all endpoints in all toxicity tests conducted for the ARCS program are equivalent. We used this approach because it is analogous to the procedure used by USEPA (1986a) to derive the AWQC--upon which the toxic units are based--wherein toxicity test results from a broad suite of taxa are averaged to obtain mean acute and chronic values for individual contaminants. Given the equally broad array of contaminants present in the ARCS sediments, we felt that such an unbiased approach was prudent. We recognize, however, that subsequent evaluation of the model may suggest that certain test results should be weighted more heavily than others.

The toxic units approach needs further validation with other data sets spanning a broader range of conditions. The ARCS data set from which the approach was developed contained no sediments that were not toxic to some degree to all the organisms tested. In this current evaluation of the toxic units approach, the lack of sediments containing only background contaminant levels and little to no observed toxicity allows us to state only that the approach is a good measure of relative toxicity among sediment samples. Full evaluation of the effectiveness of the toxic units approach to predict sediment toxicity will require a sediment data base containing sediments with a full range of toxicity (i.e., nontoxic to extremely toxic) resulting from a wide variety of contaminants.

Ranking Approach

From our analysis, we found that it is very important how much and what type of information is included in the hazard ranking of a site. As the amount of information incorporated into the ranking process declined (i.e., Priority Master Station indicators to Master Station indicators to Reconnaissance Station indicators) the hazard ranking of the sites changed. As the information used to rank the sites changed so did both the relative hazard of the sites to the most hazardous site and the order of the sites based on relative hazard. More dramatically, when the information used to estimate the relative hazards of the sites included only the bioaccumulative compounds, only three of the six sites estimated to be the most hazardous sites using the full set of information (i.e.,

relative ranks over 30) still had relative ranks above 30. The most dramatic change occurred in the relative ranking of site 3 in Indiana Harbor; it went from a relative hazard rank greater than 57 using the full set of information to less than 12 using only bioaccumulatives.

The minimal amount of information necessary for an appropriate assessment of the relative hazard among a set of sites seems to be the Master Station level (i.e., chemistry, moderate range of laboratory toxicity data, and benthic community structure). The information gained by the inclusion of macrophytes and toxicity tests with more species of invertebrates (i.e., Priority Master Stations) had little to no effect on relative hazard ranking of the sites. If only Microtox and a short list of contaminants (i.e., Reconnaissance Station data) are used to produce the relative hazard ranking for a set of sites, the relative ranking of the sites becomes confused.

Not only the amount of information, as discussed, but also the type of information used to construct the relative hazard ranking of a set of sites may dramatically affect the resulting hazard ranking. If the intent of using the ranking process is to determine overall relative toxicity, the set of information used should include all the types of information collected at Master Stations in this study (i.e., chemistry, laboratory toxicity, and benthic community structure). If the intent of using the ranking process is to determine hazard to organisms on the upper end of the aquatic food chain, including wildlife, the set of information would be similar to the bioaccumulatives tested in this study. Thus, it is crucial that the question of

concern for a set of sites be correctly formulated before such a relative ranking process is employed.

The purpose of the described ranking process is to allow different types of data, measured on different scales, to be combined into one overall estimate of relative hazard for the set of contaminated sites under investigation. The scaling done for each class of data (i.e., chemistry, laboratory toxicity, benthic community) allows for the incorporation into the estimates of relative hazard as much information as is available in the scientific literature. The result is a current best estimate of relative hazard for the sites under investigation. This approach enables the comparison and combination of sediment contamination information, measured on different scales, on one relative scale that has a foundation in environmental chemistry, toxicology, and ecology. The process is also dynamic; as more information becomes available about sediment processes, chemical fates, toxicity, etc., new information can be incorporated into the ranking model. Thus, the estimates of relative hazard become more accurate as the base of knowledge increases. It can also become a planning tool by pointing out where information is most needed.

If not already apparent, the relative site rankings generated in this study are based on contaminant levels at one point in space. The next step would be to adjust (i.e., weight) the toxicity of each site based on an estimate of the area (or volume) of contaminated sediment at each site. Thus, the single point relative hazard ranking of sites may change dramatically if less toxic sites represent a

greater proportional area (or volume).

Finally, the ranking process need not be limited to the types of data described here. Other classes of information (i.e., potential for resuspension, aesthetics, recreational potential, etc.) can also be incorporated by scaling the observed values from 1 to 100 as was done with the information presented in this report. The model can also be extended to other quantifiable hazards, such as carcinogenicity, by defining a toxic unit to be the level of concern for such hazards. Again, this demonstrates the general utility of the ranking process as one way of assessing the relative hazard among many sites when limited resources require prioritization.

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Table 1. Octanol/water partition coefficients used in the toxic units model for the contaminants measured in ARCS sediments.

Contaminant	Octanol/water Partition Coefficient (Log(K_{ow}))	Reference
Organochlorine compounds		
Chlorodioxins		
2,3,7,8-Tetrachlorodibenzodioxin	6.42	Sijm et al. 1989
1,2,3,7,8-Pentachlorodibenzodioxin	6.64	Sijm et al. 1989
1,2,3,4,7,8-Hexachlorodibenzodioxin	7.80	Sijm et al. 1989
1,2,3,6,7,8-Hexachlorodibenzodioxin	7.80	1,2,3,4,7,8-Hexachlorodibenzodioxin--Sijm et al. 1989
1,2,3,7,8,9-Hexachlorodibenzodioxin	7.80	1,2,3,4,7,8-Hexachlorodibenzodioxin--Sijm et al. 1989
1,2,3,4,6,7,8-Heptachlorodibenzodioxin	8.00	Sijm et al. 1989
Octachlorodibenzodioxin	8.00	Sijm et al. 1989
Chlorodibenzofurans		
2,3,7,8-Tetrachlorodibenzofuran	6.53	Sijm et al. 1989
1,2,3,7,8-Pentachlorodibenzofuran	6.79	Sijm et al. 1989
2,3,4,7,8-Pentachlorodibenzofuran	6.92	Sijm et al. 1989
1,2,3,4,7,8-Hexachlorodibenzofuran	7.80	1,2,3,4,7,8-Hexachlorodibenzodioxin--Sijm et al. 1989

Contaminant	Octanol/water Partition Coefficient (Log(K_{ow}))	Reference
1,2,3,6,7,8-Hexachlorodibenzofuran	7.80	1,2,3,4,7,8-Hexachlorodibenzodioxin--Sijm et al. 1989
2,3,4,6,7,8-Hexachlorodibenzofuran	7.80	1,2,3,4,7,8-Hexachlorodibenzodioxin--Sijm et al. 1989
1,2,3,7,8,9-Hexachlorodibenzofuran	7.80	1,2,3,4,7,8-Hexachlorodibenzodioxin--Sijm et al. 1989
1,2,3,4,6,7,8-Heptachlorodibenzofuran	7.92	Sijm et al. 1989
1,2,3,4,7,8,9-Heptachlorodibenzofuran	7.92	Sijm et al. 1989
Octachlorodibenzofuran	7.97	Sijm et al. 1989
Chlorobenzenes		
1,2-Dichlorobenzene	3.483 (n = 6)	USEPA 1987a
1,3-Dichlorobenzene	3.507 (n = 6)	USEPA 1987a
1,4-Dichlorobenzene	3.455 (n = 8)	USEPA 1987a
Polychlorinated biphenyls		
Aroclor® 1016	5.58 (n = 3)	USEPA 1987a
Aroclor® 1221	4.045 (n = 2)	USEPA 1987a
Aroclor® 1232	3.87 (n = 2)	USEPA 1987a
Aroclor® 1242	4.845 (n = 2)	USEPA 1987a
Aroclor® 1248	5.933 (n = 4)	USEPA 1987a
Aroclor® 1254	6.123 (n = 3)	USEPA 1987a
Aroclor® 1260	6.80 (n = 3)	USEPA 1987a
Pesticides		
Aldrin	5.30	USEPA 1987a
Cis-chlordane	4.13 (n = 2)	Chlordane USEPA 1987a

Contaminant	Octanol/water Partition Coefficient (Log(K_{ow}))	Reference
Trans-chlordane	4.13 (n = 2)	Chlordane USEPA 1987a
p,p-DDD	6.11 (n = 2)	USEPA 1987a
p,p-DDE	6.013 (n = 4)	USEPA 1987a
p,p-DDT	5.695 (n = 6)	USEPA 1987a
Dieldrin	3.54	USEPA 1987a
α-Endosulfan	-1.70	USEPA 1987a
β-Endosulfan	-1.70	USEPA 1987a
Endosulfan-sulfate	-1.30	USEPA 1987a
Endrin	4.827 (n = 3)	USEPA 1987a
Endrin aldehyde	3.15	USEPA 1987a
Endrin ketone	3.15	Endrin aldehyde USEPA 1987a
Heptachlor	4.41	USEPA 1987a
Heptachlor epoxide	2.65	USEPA 1987a
γ-Hexachlorocyclohexane (Lindane)	3.573 (n = 3)	USEPA 1987a
Methyoxychlor	4.24 (n = 2)	USEPA 1987a
Toxaphene	3.30 (n = 2)	USEPA 1987a
Polycyclic aromatic Compounds		
Acenaphthylene	3.895 (n = 2)	USEPA 1987a
Anthracene	4.477 (n = 6)	USEPA 1987a
Benz(a)anthracene	5.61 (n = 2)	USEPA 1987a
Benzo(a)pyrene	5.383 (n = 3)	USEPA 1987a
Benzo(g,h,i)perylene	6.863 (n = 3)	USEPA 1987a
Benzo(k)fluoranthene	6.45 (n = 2)	USEPA 1987a
Chrysene	5.71 (n = 3)	USEPA 1987a

Contaminant	Octanol/water Partition Coefficient (Log(K_{ow}))	Reference
Dibenzofuran	4.09	USEPA ASTER database 1993
Fluoranthene	5.150 (n = 3)	USEPA 1987a
Fluorene	4.118 (n = 4)	USEPA 1987a
Indeno(1,2,3-c,d)pyrene	7.085 (n = 2)	USEPA 1987a
Napthalene	3.341 (n = 7)	USEPA 1987a
Phenanthrene	4.524 (n = 5)	USEPA 1987a
Pyrene	5.119 (n = 8)	USEPA 1987a
Phthalate esters		
Bis(2-ethylhexyl)phthalate	9.17 (n = 2)	USEPA 1987a
Butyl benzyl phthalate	5.556 (n = 4)	USEPA 1987a
Dimethyl phthalate	1.763 (n = 3)	USEPA 1987a
Organo-metals		
Tributyltin	3.2	Maguire et al. 1983

[1]N equals number of values averaged (arithmetic mean) to produce the indicated value.

Table 2. Estimation of the chronically toxic pore-water concentration defining a toxic unit for each contaminant used in the toxic units model. "MT" minimal or no observed toxicity.

Contaminant	Toxic Unit Calculations (ug/L)	Reference
Organochlorine Compounds		
Chlorodioxins		
2,3,7,8-Tetrachlorodibenzodioxin	$0.014^{1} \times 0.0000099^{2} = 0.0000376$	USEPA 1980a and Smith et al. 1990
1,2,3,7,8-Pentachlorodibenzodioxin	$0.014^{1} \times (0.0000099/0.0087)^{3} = 0.0000160$	USEPA 1980a and Smith et al. 1990
1,2,3,4,7,8-Hexachlorodibenzodioxin	$0.014^{1} \times (0.0000099/0.045)^{3} = 0.00000308$	USEPA 1980a and Smith et al. 1990
1,2,3,6,7,8-Hexachlorodibenzodioxin	$0.014^{1} \times (0.0000099/0.004)^{3} = 0.0000348$	USEPA 1980a and Smith et al. 1990
1,2,3,7,8,9-Hexachlorodibenzodioxin	$0.014^{1} \times (0.0000099/0.0037)^{3} = 0.0000376$	USEPA 1980a and Smith et al. 1990
1,2,3,4,6,7,8-Heptachlorodibenzodioxin	$0.014^{1} \times (0.0000099/0.0028)^{3} = 0.0000495$	USEPA 1980a and Smith et al. 1990
Octachlorodibenzodioxin	$0.014^{1} \times (0.0000099/0.1)^{4} = 0.00000139$	USEPA 1980a, Smith et al. 1990, and Safe 1990
Chlorodibenzofurans		
2,3,7,8-Tetrachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.025)^{3} = 0.00000556$	USEPA 1980a and Smith et al. 1990

Contaminant	Toxic Unit Calculations (ug/L)	Reference
1,2,3,7,8-Pentachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.038)^{3}$ = 0.00000366	USEPA 1980a and Smith et al. 1990
2,3,4,7,8-Pentachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.38)^{3}$ = 0.000000366	USEPA 1980a and Smith et al. 1990
1,2,3,4,7,8-Hexachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.27)^{3}$ = 0.000000515	USEPA 1980a and Smith et al. 1990
1,2,3,6,7,8-Hexachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.065)^{3}$ = 0.00000214	USEPA 1980a and Smith et al. 1990
1,2,3,7,8,9-Hexachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.1)$ = 0.00000139	USEPA 1980a, Smith et al. 1990, and Safe 1990
2,3,4,6,7,8-Hexachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.14)^{3}$ = 0.000000993	USEPA 1980a and Smith et al. 1990
1,2,3,4,6,7,8-Heptachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.1)^{4}$ = 0.00000139	USEPA 1980a, Smith et al. 1990, and Safe 1990
1,2,3,4,7,8,9-Heptachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.1)^{4}$ = 0.00000139	USEPA 1980a, Smith et al. 1990, and Safe 1990
Octachlorodibenzofuran	$0.014^{1} \times (0.0000099/0.1)^{4}$ = 0.00000139	USEPA 1980a, Smith et al. 1990, and Safe 1990
Chlorobenzenes		
1,2-Dichlorobenzene	7.0	Michigan DNR 1993
1,3-Dichlorobenzene	180.0	Michigan DNR 1993
1,4-Dichlorobenzene	43.0	Michigan DNR 1993

Contaminant	Toxic Unit Calculations (ug/L)	Reference
Polychlorinated byphenyls (PCBs)		
Aroclor® 1016	MT	Smith et al. 1990
Aroclor® 1221	MT	Smith et al. 1990
Aroclor® 1232	$0.014^{1} \times (0.0000099/ 0.001934)^{3} = 0.0000717$	USEPA 1980a and Smith et al. 1990
Aroclor® 1242	$0.014^{1} \times (0.0000099/0.0000137)^{3} = 0.0101$	USEPA 1980a and Smith et al. 1990
Aroclor® 1248	$0.014^{1} \times (0.0000099/0.0000173)^{3} = 0.00801$	USEPA 1980a and Smith et al. 1990
Aroclor® 1254	0.014	USEPA 1980a
Aroclor® 1260	MT	Smith et al. 1990
Pesticides		
Aldrin	0.0019	Dieldrin USEPA 1980b
cis-Chlordane	0.0043	Chlordane USEPA 1980c
trans-Chlordane	0.0043	Chlordane USEPA 1980c
p,p'-DDD	0.001	DDT USEPA 1980d
p,p'-DDE	0.001	DDT USEPA 1980d
p,p'-DDT	0.001	USEPA 1980d
Dieldrin	0.0019	USEPA 1980b
α-Endosulfan	0.056	Endosulfan USEPA 1980e

Contaminant	Toxic Unit Calculations (ug/L)	Reference
β-Endosulfan	0.056	Endosulfan USEPA 1980e
Endosulfan sulfate	0.056	Endosulfan USEPA 1980e
Endrin	0.0023	USEPA 1980f
Endrin aldehyde	0.0023	Endrin USEPA 1980f
Endrin ketone	0.0023	Endrin USEPA 1980f
Heptachlor	0.0038	USEPA 1980g
Heptachlor epoxide	0.0038	Heptechlor USEPA 1980g
γ-Hexachlorocyclohexane (Lindane)	0.08	USEPA 1980h
Methyoxychlor	0.03	USEPA 1976
Toxaphene	0.0002	USEPA 1986b
Polycyclic aromatic hydrocarbons (PAHs)		
Acenaphthylene	24000 $ug/kg^5/(0.04^6 \times K_{oc}^7)$	USEPA 1985a and DiToro et al. 1991
Anthracene	44000 $ug/kg^5/(0.04^6 \times K_{oc}^7)$	USEPA 1985a and DiToro et al. 1991
Benz(a)anthracene	220000 $ug/kg^5/(0.04^6 \times K_{oc}^7)$	USEPA 1985a and DiToro et al. 1991
Benzo(a)pyrene	1800000 $ug/kg^5/(0.04^6 \times K_{oc}^7)$	USEPA 1985a and DiToro et al. 1991

Contaminant	Toxic Unit Calculations (ug/L)	Reference
Benzo(g,h,i)perylene	(1800000 ug/kg[5]/(0.04[6] x K_{oc}[7])) x 3.11[8]	USEPA 1985a, DiToro et al. 1991, and Newsted and Giesy 1987
Benzo(k)fluoranthene	5000000 ug/kg[5]/(0.04[6] x K_{oc}[7])	USEPA 1985a and DiToro et al. 1991
Chrysene	460000 ug/kg[5]/(0.04[6] x K_{oc}[7])	USEPA 1985a and DiToro et al. 1991
Dibenzofuran	7[9] x 0.708[10] = 4.956	1,2-Dichlorobenzene Michigan DNR 1993 and LeBlanc 1980
Fluoranthene	(1800000 ug/kg[5]/(0.04[6] x K_{oc}[7])) x 2.43[8]	USEPA 1985a, DiToro et al. 1991, and Newsted and Giesy 1987
Fluorene	28000 ug/kg[5]/(0.04[6] x K_{oc}[7])	USEPA 1985a and DiToro et al. 1991
Indeno(1,2,3-c,d)pyrene	24000000 ug/kg[5]/(0.04[6] x K_{oc}[7])	USEPA 1985a and DiToro et al. 1991
Napthalene	29.0	Michigan DNR 1993
Phenanthrene	56000 ug/kg[5]/(0.04[6] x K_{oc}[7])	USEPA 1985a and DiToro et al. 1991
Pyrene	198000 ug/kg[5]/(0.04[6] x K_{oc}[7])	USEPA 1985a and DiToro et al. 1991

Contaminant	Toxic Unit Calculations (ug/L)	Reference
Phthalate esters		
Bis(2-ethylhexyl)phthalate	$7^{9} \times 4.583^{10} = 32.081$	1,2-Dichlorobenzene Michigan DNR 1993 and LeBlanc 1980
Butyl benzyl phthalate	3.0	USEPA 1980i
Dimethyl phthalate	$7^{9} \times 13.75^{10} = 96.25$	1,2-Dichlorobenzene Michigan DNR 1993 and LeBlanc 1980
Metals, organo-metals, and metaloids		
Arsenic	190.0	USEPA 1984a
Cadmium	$e^{(0.7852 \times \ln(\text{hardness}) - 3.49)}$	USEPA 1984b
Chromium	$e^{(0.819 \times \ln(\text{hardness}) + 1.561)}$	USEPA 1984c
Copper	5.6	USEPA 1980j
Iron	1000	USEPA 1976
Lead	$e^{(1.273 \times \ln(\text{hardness}) - 4.705)}$	USEPA 1984d
Manganese	not toxic	USEPA 1976
Mercury	0.012	USEPA 1984e
Methyl mercury	$0.012^{11}/10^{12} = 0.0012$	Mercury USEPA 1980k and USEPA 1984e
Nickel	$e^{(0.846 \times \ln(\text{hardness}) + 1.1645)}$	USEPA 1986c
Selenium	1.0 (ug/g dry weight sediment)	Lemly et al. 1993

Contaminant	Toxic Unit Calculations (ug/L)	Reference
Silver	29.0	Michigan DNR 1993
Tributyl tin	0.009	Michigan DNR 1993
Zinc	$e^{(0.8473 \times \ln(\text{hardness}) + 0.7614)}$	USEPA 1987b
Other compounds		
Ammonia	((0.8/FT[13])/FPH[14])/RATIO[15]	USEPA 1985b

[1]Aroclor® 1254 chronic AWQC (USEPA 1980a).
[2]AHH activity of Aroclor® 1254 relative to that of 2,3,7,8-Tetrachlorodibenzodioxin (Smith et al. 1990).
[3]The ratio AHH activity of Aroclor® 1254 relative to 2,3,7,8-Tetrachlorodibenzodioxin:AHH activity of listed contaminant relative to 2,3,7,8-Tetrachlorodibenzodioxin (Smith et al. 1990).
[4]The ratio AHH activity of Aroclor® 1254 relative to 2,3,7,8-Tetrachlorodibenzodioxin (Smith et al. 1990):Toxic Equivalency Factor (TEF) of listed contaminant relative to 2,3,7,8-Tetrachlorodibenzodioxin (Safe 1990).
[5]Estimated sediment threshold concentration for listed contaminant (USEPA 1985a).
[6]Proportion of organic carbon in sediment used to estimate sediment threshold concentrations (USEPA 1985a).
[7]$K_{OC} = 10^{(0.00028 + 0.983 * \log(KOW))}$, K_{OW} is octanol/water partition coefficient (DiToro et al. 1991).
[8]Relative toxicity of listed contaminant to Benzo(a)pyrene (Newstead and Giesy 1987).
[9]1,2-Dichlorobenzen 1993 water quality standard from Michigan Department of Natural Resources.
[10]Relative toxicity of listed contaminat to1,2-Dichlorobenzene (LeBlanc 1980).
[11]AWQC for mercury (USEPA 1984e).
[12]Relative toxicity of methyl mercury to mercury (USEPA 1980k).
[13]$FT = 10^{(0.03 \times (20 - 15))}$.
[14]FPH = 1, IF pH < = 8 THEN FPH = $(1 + 10^{(7.4 - pH)})/1.25$.
[15]RATIO = 16, IF pH < = 7.7 THEN RATIO = $24 \times 10^{(7.7 - pH)}/(1 + 10^{(7.4 - pH)})$.

Table 3. Laboratory toxicity tests included in the assessment of sediment toxicity. Laboratory toxicity tests used in evaluation of Master Station data are denoted by '*'.

Test Organism	Length of Test	Sediment Phase	Endpoints
Fishes			
*Pimephales promelas embryo larvae	7 d	Whole sediment	Survival, length, and terata
*Pimephales promelas larvae	7 d	Whole sediment	Survival and weight
Zooplankters			
Ceriodaphnia dubia	7 d	Sediment elutriate (6.25, 12.5, 25, 50, 100%) and whole sediment	Reproduction and survival
*Daphnia magna	48 h	Sediment elutriate (3.125, 6.25, 12.5, 25, 50, and 100%) and whole sediment	Survival
*Daphnia magna	7 d	Whole sediment	Survival and reproduction
Benthic invertebrate			
Chironomous riparius	14 d	Whole sediment	Survival and length
*Chironomous tentans	10 d	Whole sediment	Survival and length

Test Organism	Length of Test	Sediment Phase	Endpoints
*Hexagenia bilineata	10 d	Sediment elutriate and whole sediment	Survival and molting frequency
*Hyalella azteca	14 d, 28 d	Whole sediment	Survival, length, antenna length, and sexual maturation
*Hyalella azteca	7 d	Whole sediment	Survival
Pontoporeia hoyi	5 d	Whole sediment	Preference
Pontoporeia hoyi	20 d	Whole sediment	Survival
Phytoplankters			
*Selenastrum capricornutum	24 h	Sediment elutriate (6.25, 10.2, 12.5, 25, 28.6, 50, 57, 71.4%)	^{14}C uptake
*Selenastrum capricornutum	48 h	Sediment elutriate (6.25, 12.5, 25, 50, 100%)	Growth
*Selenastrum capricornutum	96 h	Sediment elutriate (6.25, 12.5, 25, 50, 100%)	Growth
Macrophytes			
Hydrilla verticillata		Whole sediment	Root length, shoot length, chlorophyll, dehydrogenase, and peroxidase

Test Organism	Length of Test	Sediment Phase	Endpoints
Lemna minor	4 d	Whole sediment	Biomass, chlorophyll a, and frond number
Microbes			
*Photobacterium phosphoreum	5 min, 15 min	Sediment elutriate (5.65, 6.25, 11.25, 12.5, 22.5, 25, 45, 50, 100%)	Luminescence

Table 4. Tolerance to pollution values for taxa identified in the full group of sediment samples used in the analyses. Also included is the associated reference from which each tolerance value was taken. Those tolerance values with an 'n' value were estimated because no value was available from any reference. An estimate was either calculated from the mean of values for the species found in the sediments (i.e. family or high taxon tolerance) or from the mean of members of the same genera with tolerance values. The values for the hemiptera were based on educated guess.

Scientific Name	Tolerance Value	Reference
Amphipoda	6.0	Hilsenhoff 1988
Crustacea		
Gammarus lacustris	6.9	Lenat 1993
Annelida		
Hirudinea	7.9 (n = 3)	Lenat 1993
Helobdella elongata	9.9	Lenat 1993
Helobdella stagnalis	6.7	Lenat 1993
Batracobdella phalera	7.1	Lenat 1993
Placobdella ornata	7.8 (n = 2)	Lenat 1993
Naididae		
Dero digitata	10	Lenat 1993
Oligocheata	8.2	Lenat 1993
Tubificidae	8.55 (n = 8)	Lenat 1993
Aulodrilus pigueti	4.7	Lenat 1993
Aulodrilus limnobius	5.2	Lenat 1993
Aulodrilus plureseta	4.95 (n = 2)	Lenat 1993
Ilyodrilus templetoni	9.4	Lenat 1993
Limnodrilus cervix	10	Lenat 1993
Limnodrilus claparedianus	9.78 (n = 4)	Lenat 1993
Limnodrilus hoffmeisteri	9.8	Lenat 1993
Limnodrilus maumeensis	9.78 (n = 4)	Lenat 1993

Scientific Name	Tolerance Value	Reference
Limnodrilus undedemianus	9.7	Lenat 1993
Limnodrilus sp.	9.6	Lenat 1993
Quistadrilus multisetosus	8.55 (n = 8)	Lenat 1993
Tubifex tubifex	10	Lenat 1993
Bivalvia		
Sphaeriidae	7.25 (n = 2)	Lenat 1993
Musculium sp.	7.25 (n = 2)	Lenat 1993
Pisidium sp.	6.8	Lenat 1993
Sphaerium sp.	7.7	Lenat 1993
Unionidae		
Anodonta imbecillis	5.4	Lenat 1993
Anodonta grandis	5.4	Lenat 1993
Eliptio complanata	5.4	Lenat 1993
Coleoptera		
Pshenidae	2.5	Lenat 1993
Haliplus	5.7	Lenat 1993
Decapoda	6.0	USEPA 1989
Diptera		
Ceratopogonidae		
Plapomyia sp.	6.9	Lenat 1993
Chaoboridae		
Chaoborus sp.	8.5	Lenat 1993
Chironomidae	5.7	Lenat 1993

Scientific Name	Tolerance Value	Reference
Chironomous sp.	9.8	Lenat 1993
Cladopelma sp.	2.5	Lenat 1993
Coelotanypus sp.	7.7	Lenat 1993
Cricotopus sp.	8.12 (n = 5)	Lenat 1993
Cryptochironomous sp.	7.35 (n = 2)	Lenat 1993
Dicrotendipes sp.	7.9	Lenat 1993
Glyptotendipes sp.	8.5	Lenat 1993
Microchironomous sp.	7.79 (n = 6)	Lenat 1993
Polypedilum sp.	6.67 (n = 7)	Lenat 1993
Procladius sp.	9.3	Lenat 1993
Tanypus sp.	9.6	Lenat 1993
Ephemeroptera	2.7	Lenat 1993
Caenis sp.	7.6	Lenat 1993
Gastropoda		
Ancylida		
Laevapex fucus	7.3	Lenat 1993
Bithyniidae		
Bithynia tentaculata	6.1	Lenat 1993 (Mullusca)
Hydrobiidae		
Cincinnatia cincinnatiensis	6.1	Lenat 1993 (Mullusca)

Scientific Name	Tolerance Value	Reference
Valvatidae		
Valvata lewisi	6.1	Lenat 1993 (Mollusca)
Valvata tricarinata	6.1	Lenat 1993 (Mollusca)
Hemiptera	6.0	(estimate)
Sigara sp.	6.0	(estimate)
Odanata	6.9	Lenat 1993
Gomphus sp.	6.2	Lenat 1993
Trichoptera		
Oecetis sp.	5.7	Lenat 1993

Table 5. Bioaccumulative Contaminants of Concern[1] used in toxic units model

Organochlorine compounds	Polychlorinated biphenyls	**Polycyclic aromatic hydrocarbons (PAHs)**
Chlorodioxins and furans	Aroclor® 1016	Benzo(a)pyrene
2,3,7,8-Tetrachlorodibenzodioxin	Aroclor® 1221	Benzo(g,h,i)perylene
1,2,3,7,8-Pentachlorodibenzodioxin	Aroclor® 1232	Benzo(k)fluoranthene
1,2,3,4,7,8-Hexachlorodibenzodioxin	Aroclor® 1242	Endrin
1,2,3,6,7,8-Hexachlorodibenzodioxin	Aroclor® 1248	Endrin aldehyde
1,2,3,7,8,9-Hexachlorodibenzodioxin	Aroclor® 1254	Endrin ketone
1,2,3,4,6,7,8-Heptachlorodibenzodioxin	Aroclor® 1260	Heptachlor
Octachlorodibenzodioxin	**Pesticides**	Heptachlor epoxide
2,3,7,8-Tetrachlorodibenzofuran	Aldrin	γ-Hexachlorocyclo-hexane (Lindane)
1,2,3,7,8-Pentachlorodibenzofuran	cis-Chlordane	Methyoxychlor
2,3,4,7,8-Pentachlorodibenzofuran	trans-Chlordan	Toxaphene
1,2,3,4,7,8-Hexachlorodibenzofuran	p,p-DDD	**Metals, organo-metals, and metaloids**
1,2,3,6,7,8-Hexachlorodibenzofuran	p,p-DDE	Arsenic
1,2,3,7,8,9-Hexachlorodibenzofuran	p,p-DDT	Methyl mercury
2,3,4,6,7,8-Hexachlorodibenzofuran	Dieldrin	Mercury
1,2,3,4,6,7,8-Heptachlorodibenzofuran	α-Endosulfan	Selenium
1,2,3,4,7,8,9-Heptachlorodibenzofuran	β-Endosulfan	
Octachlorodibenzofuran	Endosulfan sulfate	

[1]Modified from USEPA (1993). Draft GLWQI.

Table 6. Toxic units, based on the estimated bioavailable fraction, for individual contaminants in Buffalo River sediments. Only contaminants given are those for which toxic units were one or greater at one or more sites; all contaminants included in total.

	Site				
Contaminant	BR 1	BR 3	BR 7	BR 8	BR 9
Ammonia (unionized)	5.31	1.56	2.25	2.32	4.12
Chromium	NT[1]	11.13	3.11	1.77	2.39
p,p-DDT	2.06	8.24	14.74	NT	NT
β-Endosulfan	NT	NT	1128.38	NT	NT
Endrin aldehyde	NT	1033.58	NT	NT	NT
Iron	NT	984.36	701.8	514.56	449.76
Methyl mercury	581.59	NT	NT	NT	NT
Naphthalene	4.01	NT	NT	NT	NT
Octachlorodibenzo-dioxin	1.33	NT	NT	NT	NT
Aroclor® 1248	1.05	NT	NT	NT	NT
Aroclor® 1254	NT	11.50	NT	NT	NT
Selenium	3.80	NT	NT	NT	NT
Tributyl tin	23.12	NT	NT	NT	NT
Total	623.97	2051.75	1851.03	518.94	456.44

[1]NT stands for not toxic (i.e., the estimated pore-water concentration for the individual contaminant was less than the level of concern).

Table 7. Toxic units, based on the estimated bioavailable fraction, for individual contaminants in Indiana Harbor sediments. Only contaminants given are those for which toxic units were one or greater at one or more sites; all contaminants included in total.

	Site			
Contaminant	IH 3	IH 4	IH 6	IH 7
Aldrin	3.56	NT[1]	5.32	12.21
Ammonia (unionized)	7.93	8.70	12.75	16.06
Anthracene	NT	NT	NT	1.35
trans-Chlordane	17.47	NT	26.23	39.26
Chromium	97.97	63.91	85.06	779.21
p,p-DDE	NT	NT	1.06	2.94
p,p-DDT	NT	NT	2.18	NT
Dibenzofuran	NT	NT	NT	11.63
Dieldrin	637.74	NT	496.54	NT
β-Endosulfan	675.76	NT	NT	NT
Endrin aldehyde	NT	NT	195.32	NT
Heptachlor	NT	NT	10.50	44.37
Heptachlor epoxide	NT	NT	1804.79	2010.72
Iron	4719.95	3681.06	1335.52	10712.79
Methyl mercury	NT	1350.47	NT	364.63
Naphthalene	1.71	1.14	1.31	1.02
Octachlorodibenzo-dioxin	NT	NT	3.66	5.17
Octachlorodibenzo-furan	NT	NT	NT	3.85
Aroclor® 1242	223.04	90.76	353.63	836.59

Contaminant	Site IH 3	IH 4	IH 6	IH 7
Aroclor® 1254	NT	11.50	NT	NT
Selenium	2.60	2.30	3.80	3.10
Tributyl tin	249.13	154.88	1028.63	NT
Total	6645.32	5354.88	5369.41	14848.66

[1]NT stands for not toxic (i.e., the estimated pore-water concentration for the individual contaminant was less than the level of concern).

Table 8. Toxic units, based on the estimated bioavailable fraction, for individual contaminants in Saginaw River sediments. Only contaminants given are those for which toxic units were one or greater at one or more sites; all contaminants included in total.

Contaminant	Site SR 3	SR 6	SR 10
Aldrin	NT[1]	56.14	NT
Ammonia (unionized)	1.67	1.93	NT
trans-Chlordane	NT	136.31	NT
Chromium	2.98	90.73	2.31
p,p-DDE	NT	8.26	NT
Heptachlor	NT	81.84	NT
Heptachlor epoxide	NT	5965.91	NT
1234678-Heptachlorodibenzofuran	NT	1.08	NT
Iron	648.96	27.36	661.99
Octachlorodibenzo-dioxin	1.35	4.41	1.32
Octachlorodibenzo-furan	NT	1.37	NT
Aroclor® 1242	223.04	4921.87	NT
Aroclor® 1254	NT	25.96	16.20
12378-Pentachlorodibenzofuran	NT	1.76	NT
23478-Pentachlorodibenzofuran	2.17	11.21	1.29

Contaminant	Site SR 3	SR 6	SR 10
Tetrachlorodi-benzofuran	NT	6.94	NT
Tributyl tin	39.84	NT	NT
Total	699.97	11344.15	685.84

[1]NT stands for not toxic (i.e., the estimated pore-water concentration for the individual contaminant was less than the level of concern).

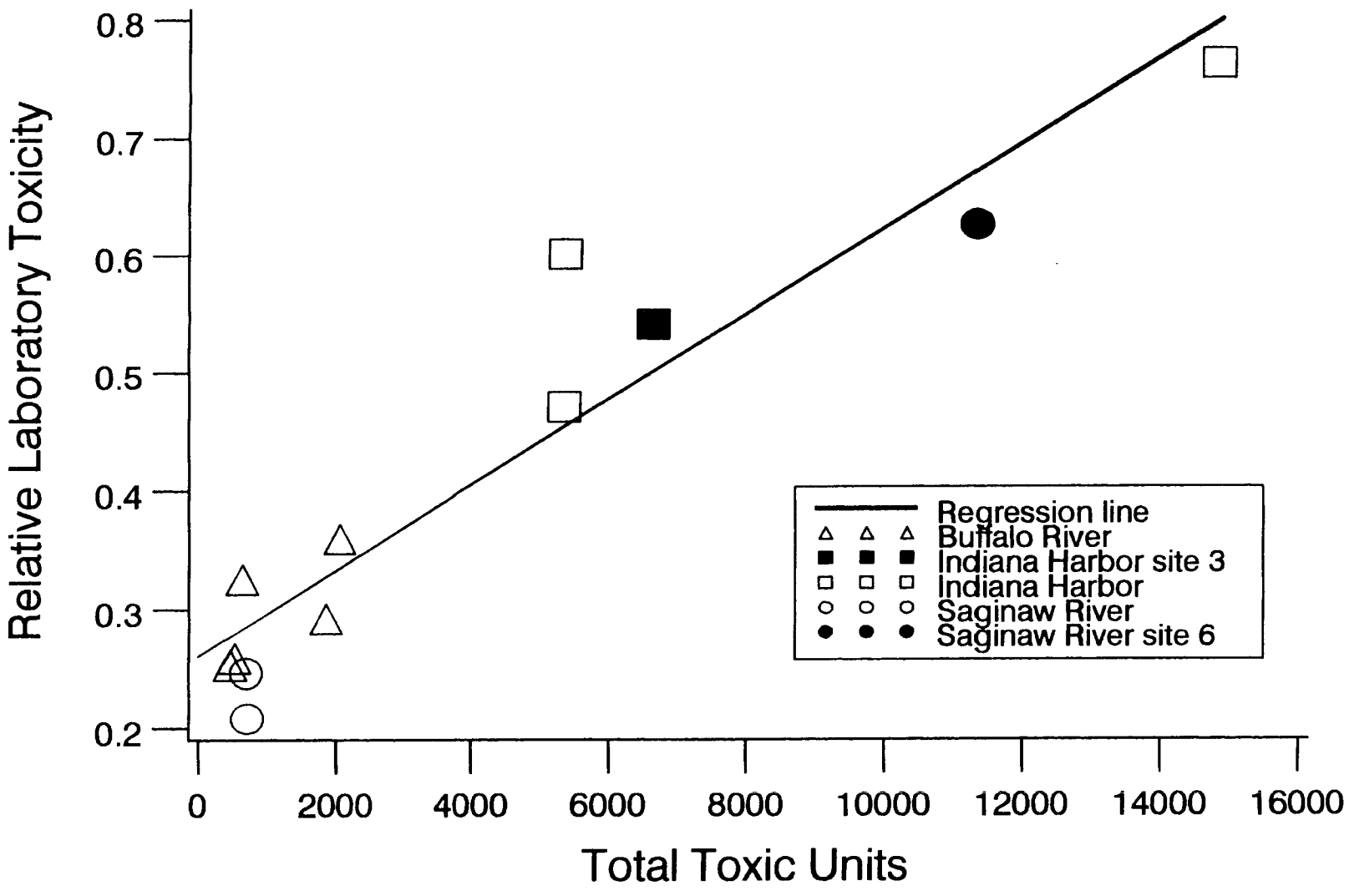

Figure 1. Observed relative sediment toxicity versus total toxic units based on bioavailable fractions of all contaminants. The line represents the relation $Y = 0.26 - 0.000036X$ (R-squared = 0.89, n = 12, P = 0.0001).

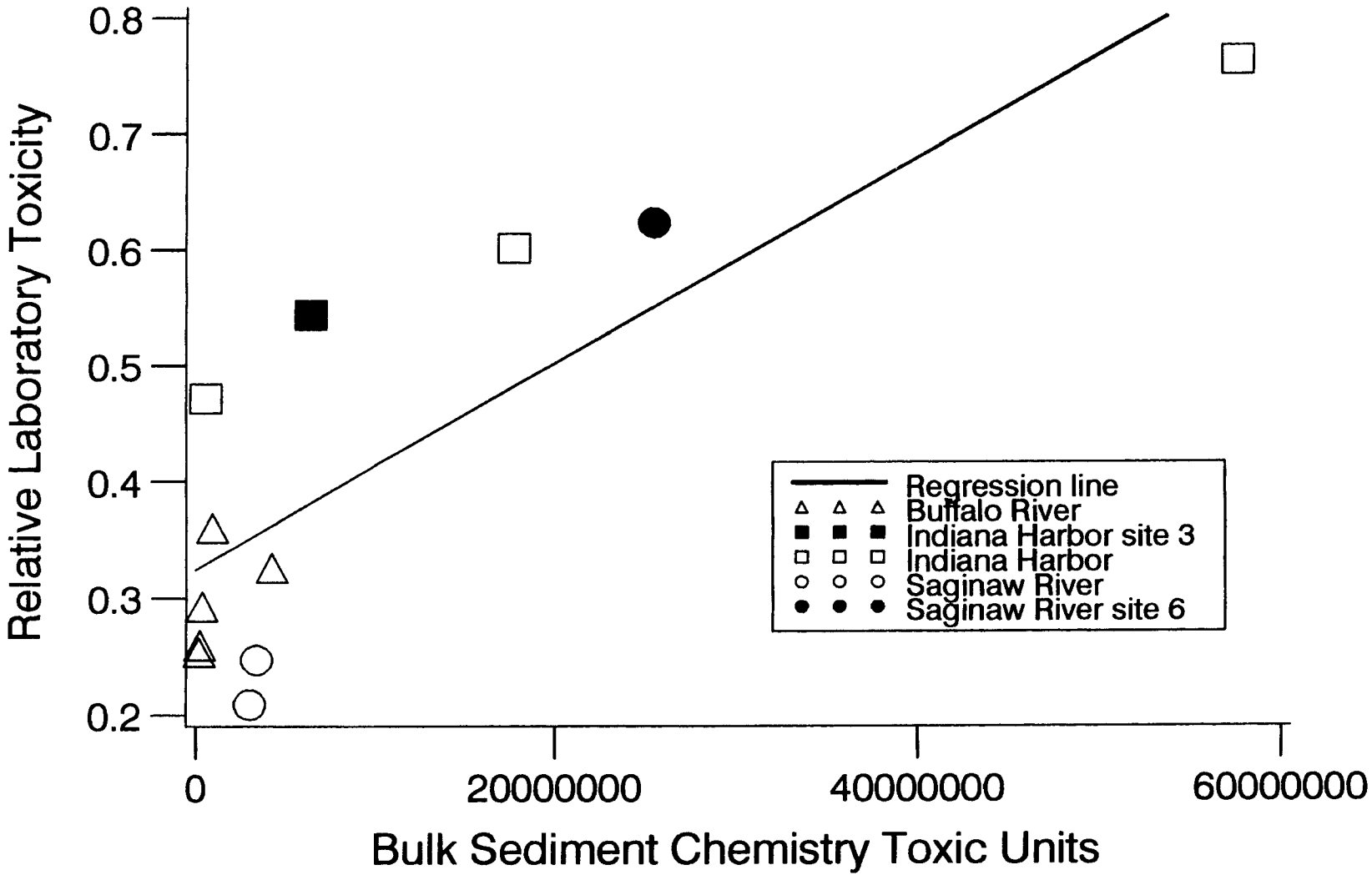

Figure 2. Observed relative sediment toxicity versus total toxic units based on bulk sediment concentrations of all contaminants. The line represents the relation Y = 0.32 - 0.0000000089X (R-squared = 0.68, n = 12, P =0.0009).

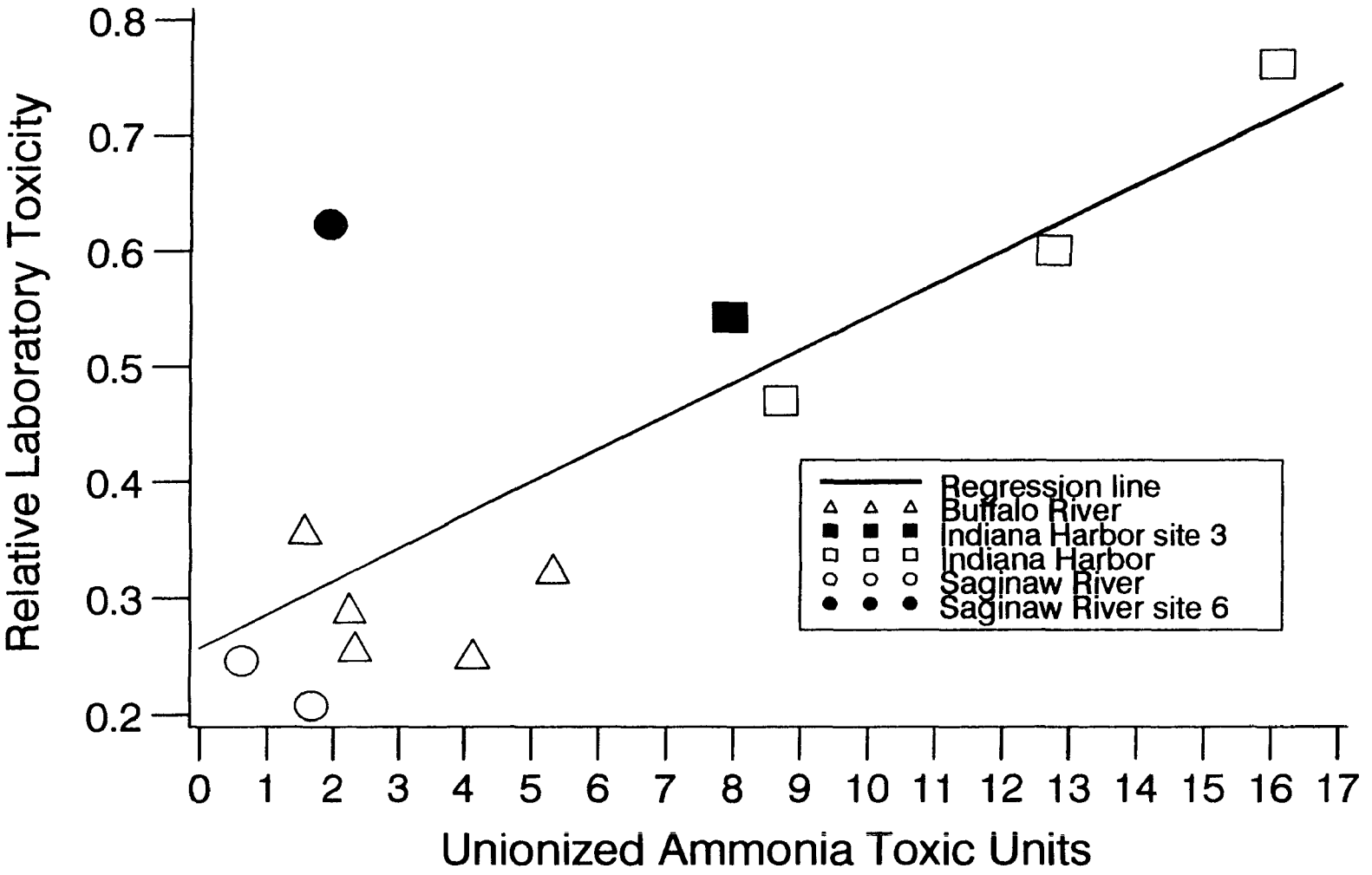

Figure 3. Observed relative sediment toxicity versus total toxic units based on unionized ammonia alone. The line represents the relation Y = 0.26 - 0.02868X (R-squared = 0.61, n = 12, P = 0.003).

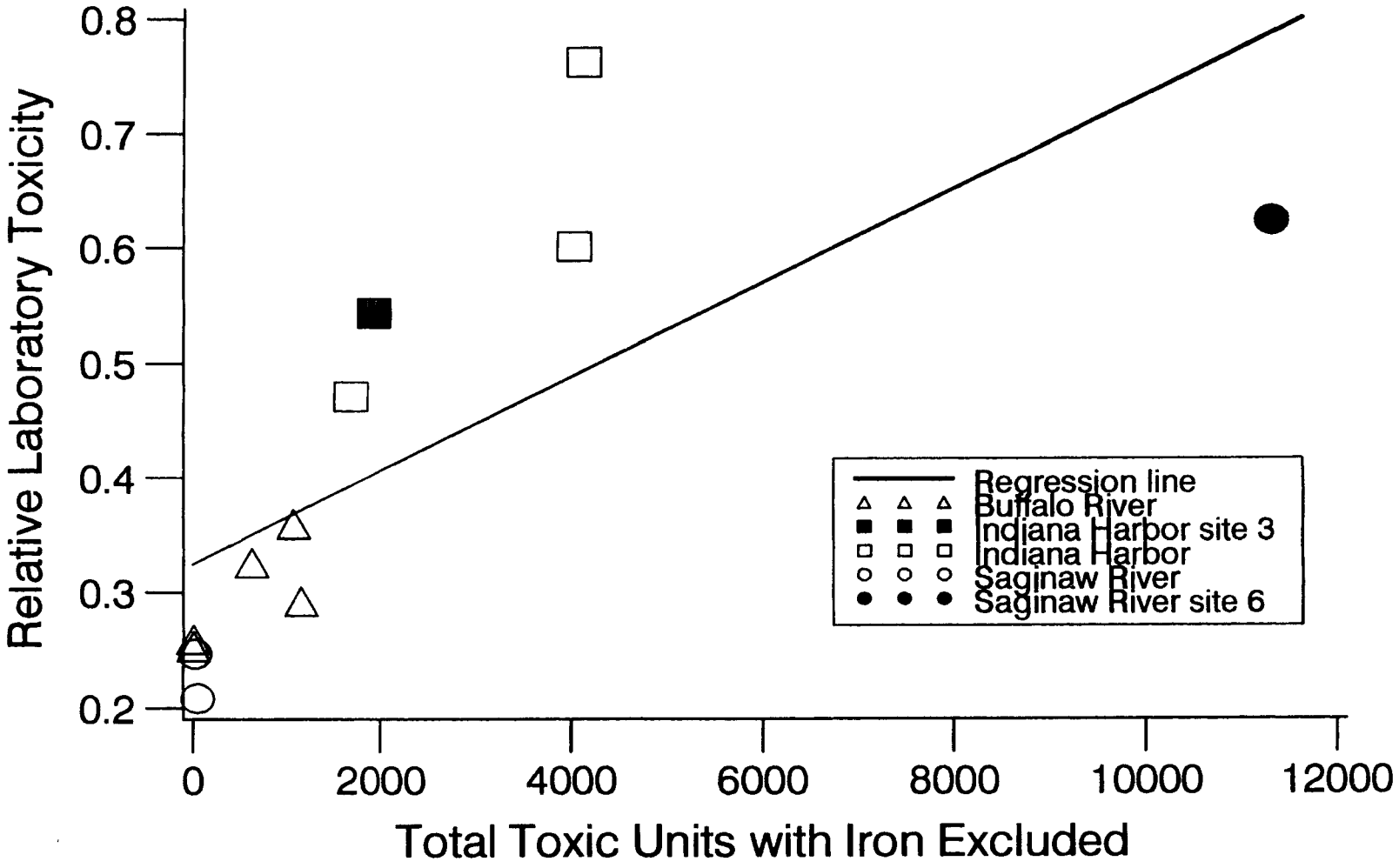

Figure 4. Observed relative sediment toxicity versus total toxic units based on bioavailable fractions of all contaminants, without iron. The line represents the relation Y = 0.32 - 0.00004X (R-squared = 0.52, n = 12, P = 0.008).

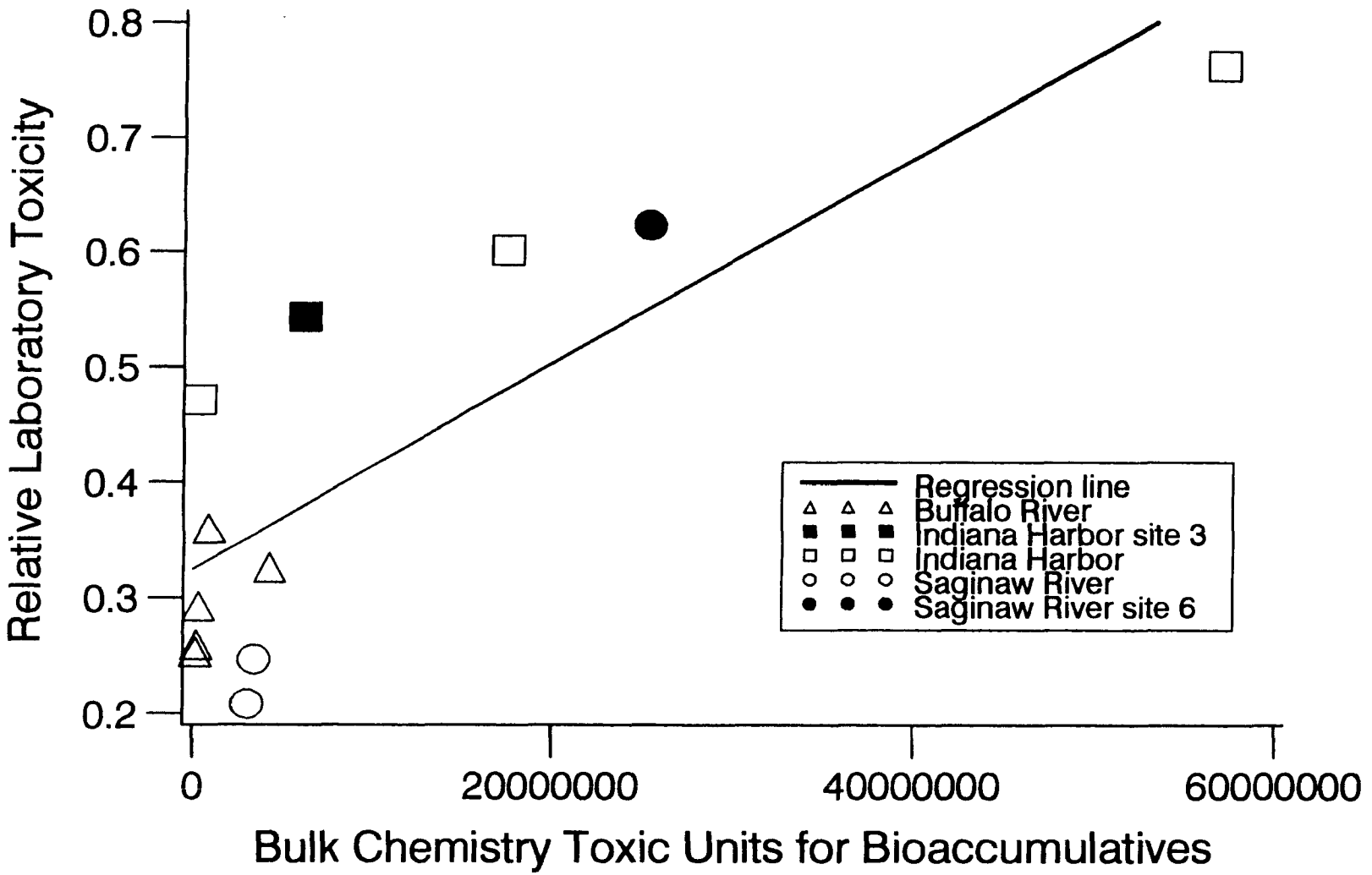

Figure 5. Observed relative sediment toxicity versus total toxic units based on bulk sediment concentrations of bioaccumulative contaminants. Line represents the relation Y = 0.32 - 0.0000000089X (R-squared = 0.68, n = 12, P = 0.001).

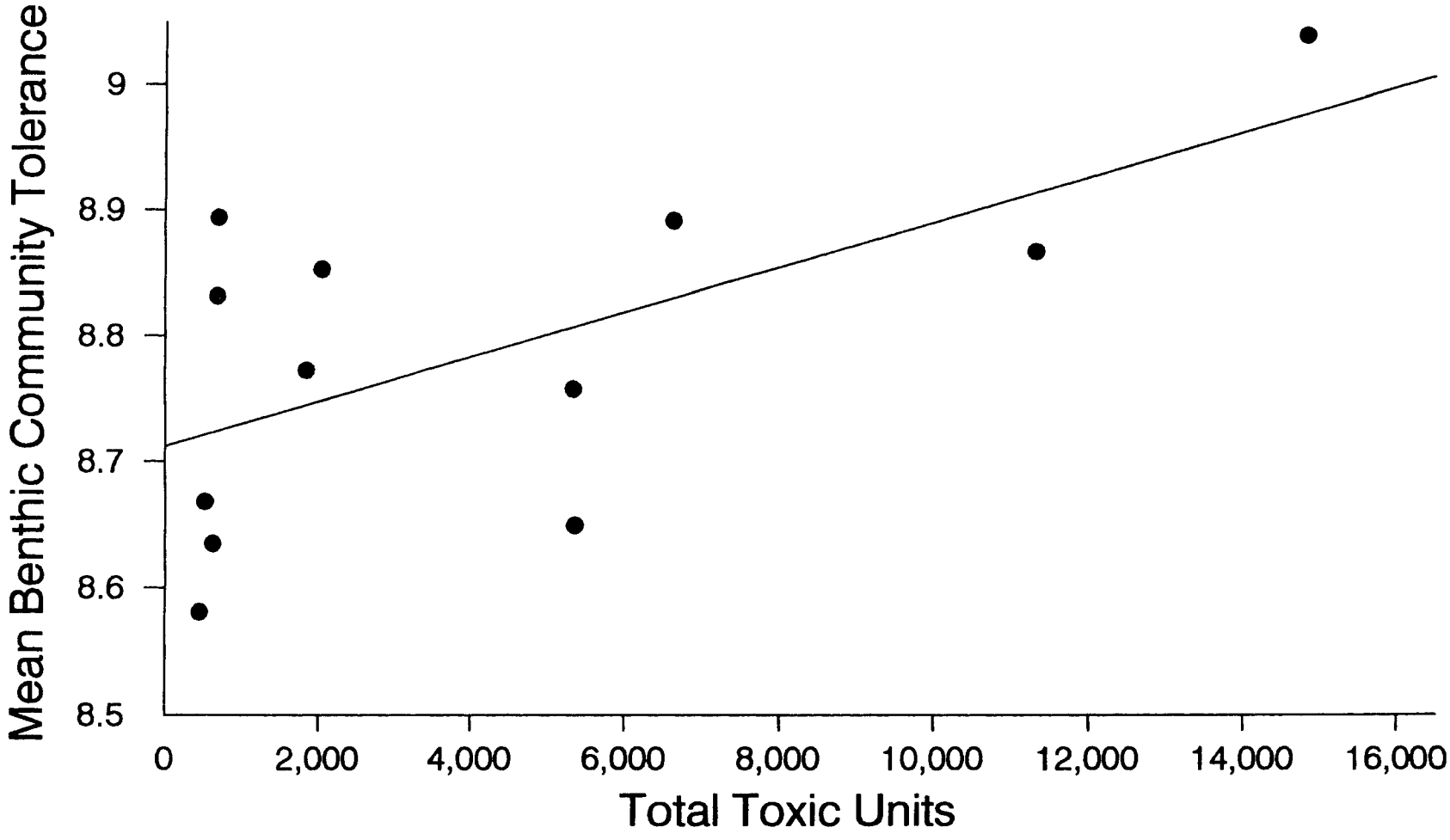

Figure 6. Benthic community mean tolerance to pollution versus total toxic units based on bioavailable fractions of all contaminants. The line represents the relation Y = 8.71 - 0.000018X (R-squared = 0.40, n = 12, P = 0.0278).

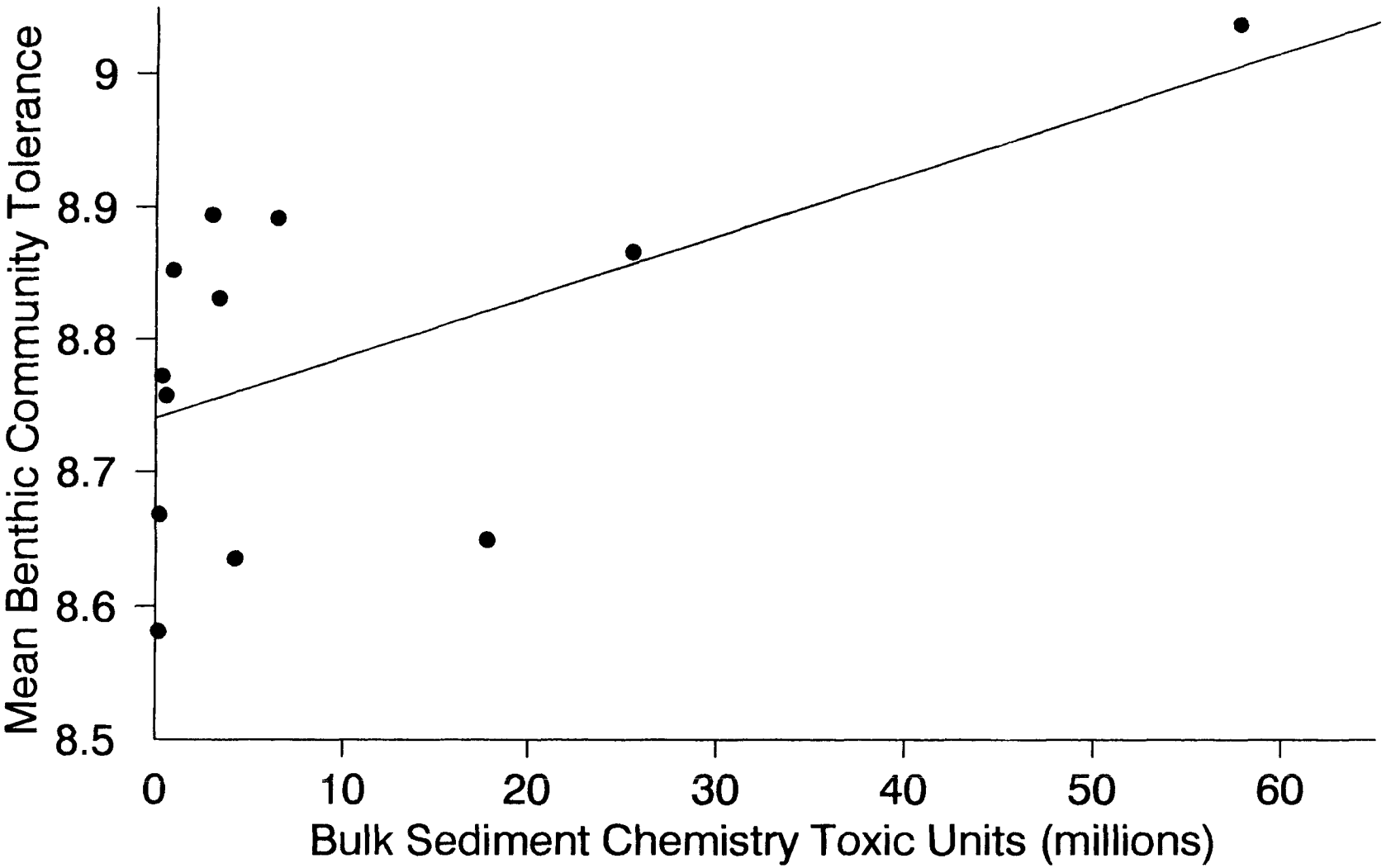

Figure 7. Benthic community mean tolerance to pollution versus total toxic units based on bulk sediment concentrations of all contaminants. The line represents the relation Y = 8.74 - 0.000000005X (R-squared = 0.34, n = 12, P = 0.0463).

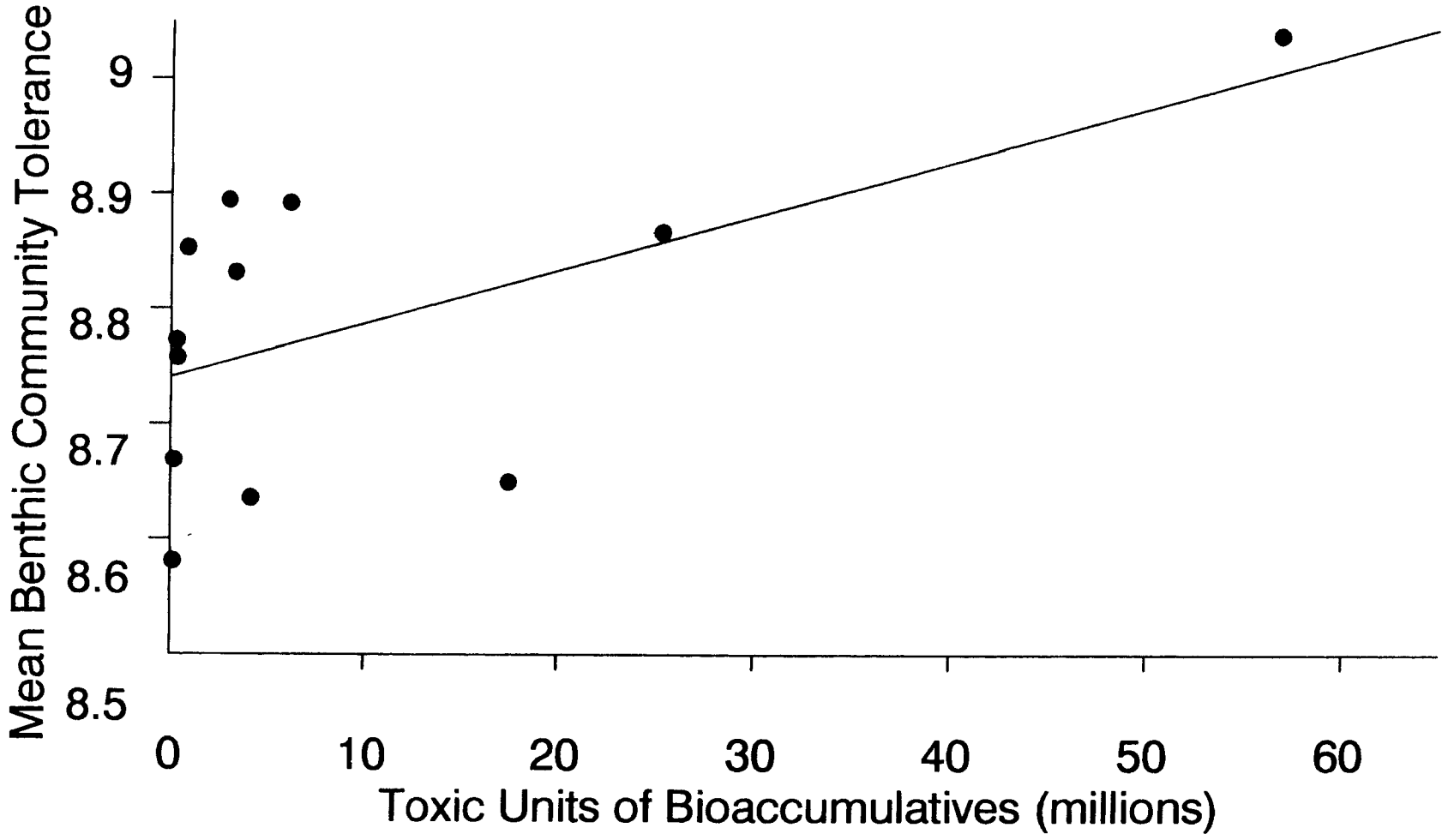

Figure 8. Benthic community mean tolerance to pollution versus total toxic units based on bulk sediment concentrations of only bioaccumulative contaminants. The line represents the relation Y = 8.74 - 0.000000005X (R-squared = 0.34, n = 12, P = 0.0466).

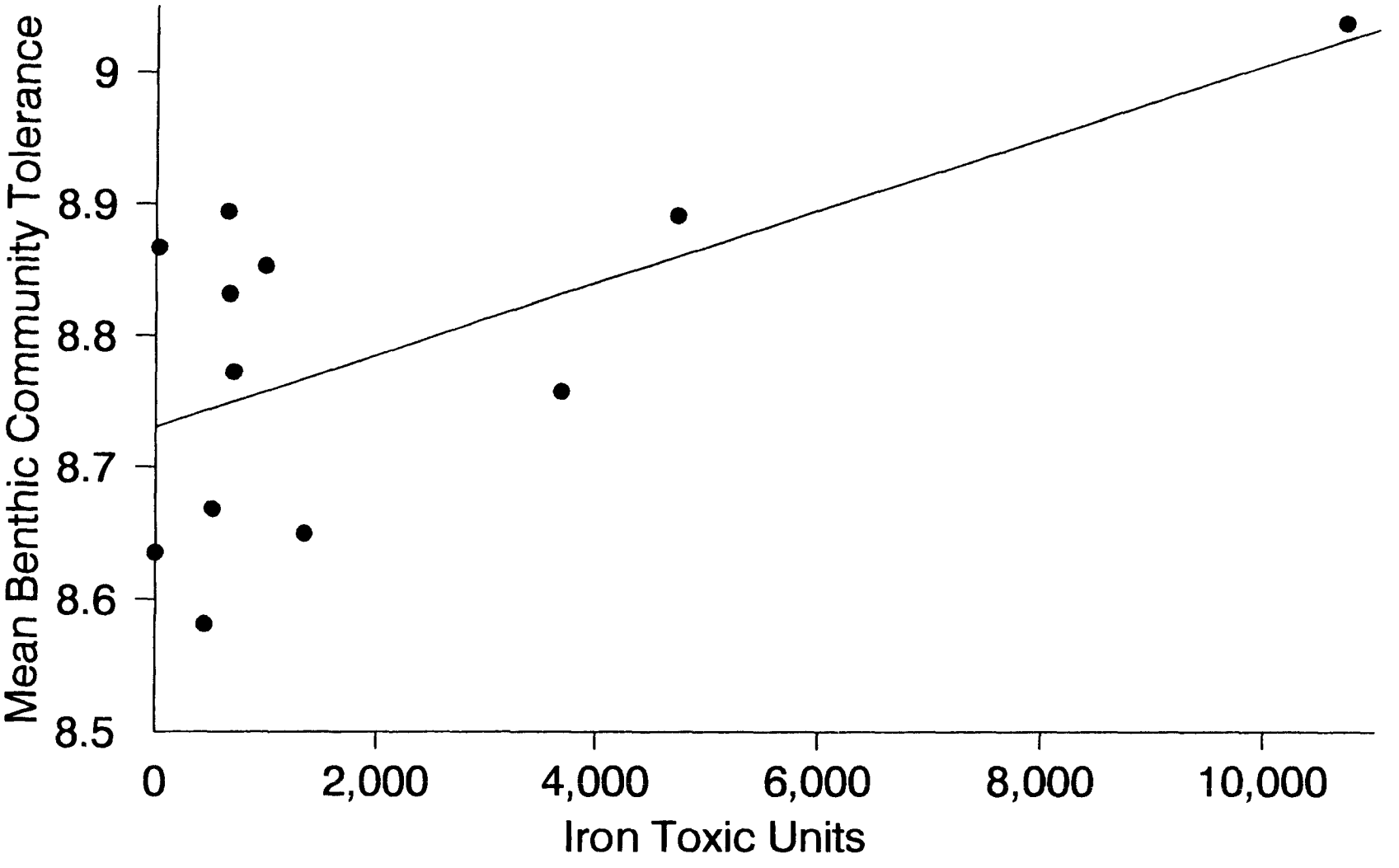

Figure 9. Benthic community mean tolerance to pollution versus total toxic units based on bioavailable fractions of iron only. The line represents the relation Y = 8.73 - 0.000027X (R-squared = 0.40, n = 12, P = 0.0261).

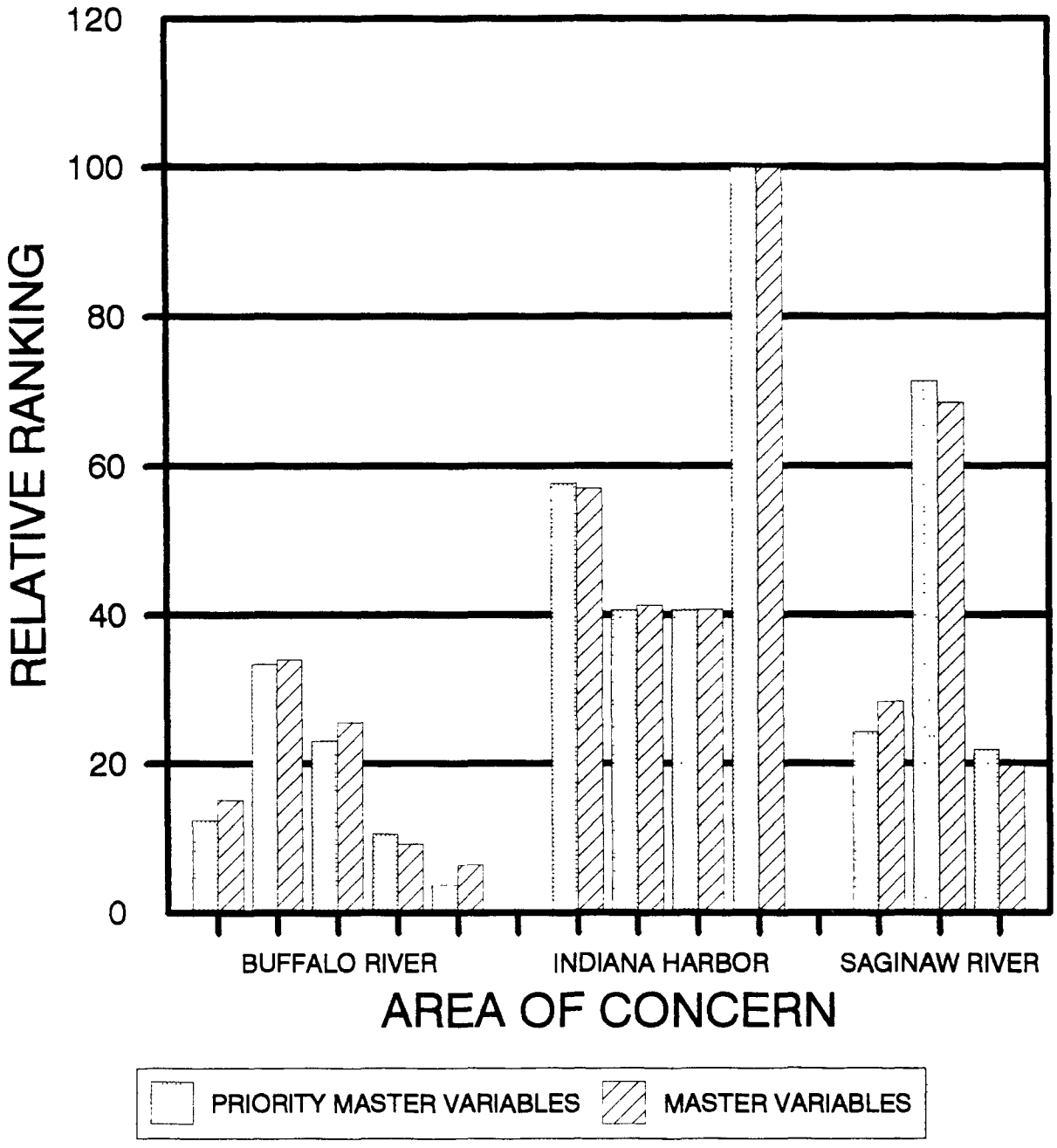

Figure 10. Comparison of the overall ranking of sites based on Priority Master Stations (shaded bars) versus Master Stations (crosshatched bars). Bars represent the average of the relative ranking among sites of toxic units, control-adjusted laboratory toxicity, and mean tolerance to pollution of the benthic community for both Priority Master Stations and Master Stations.

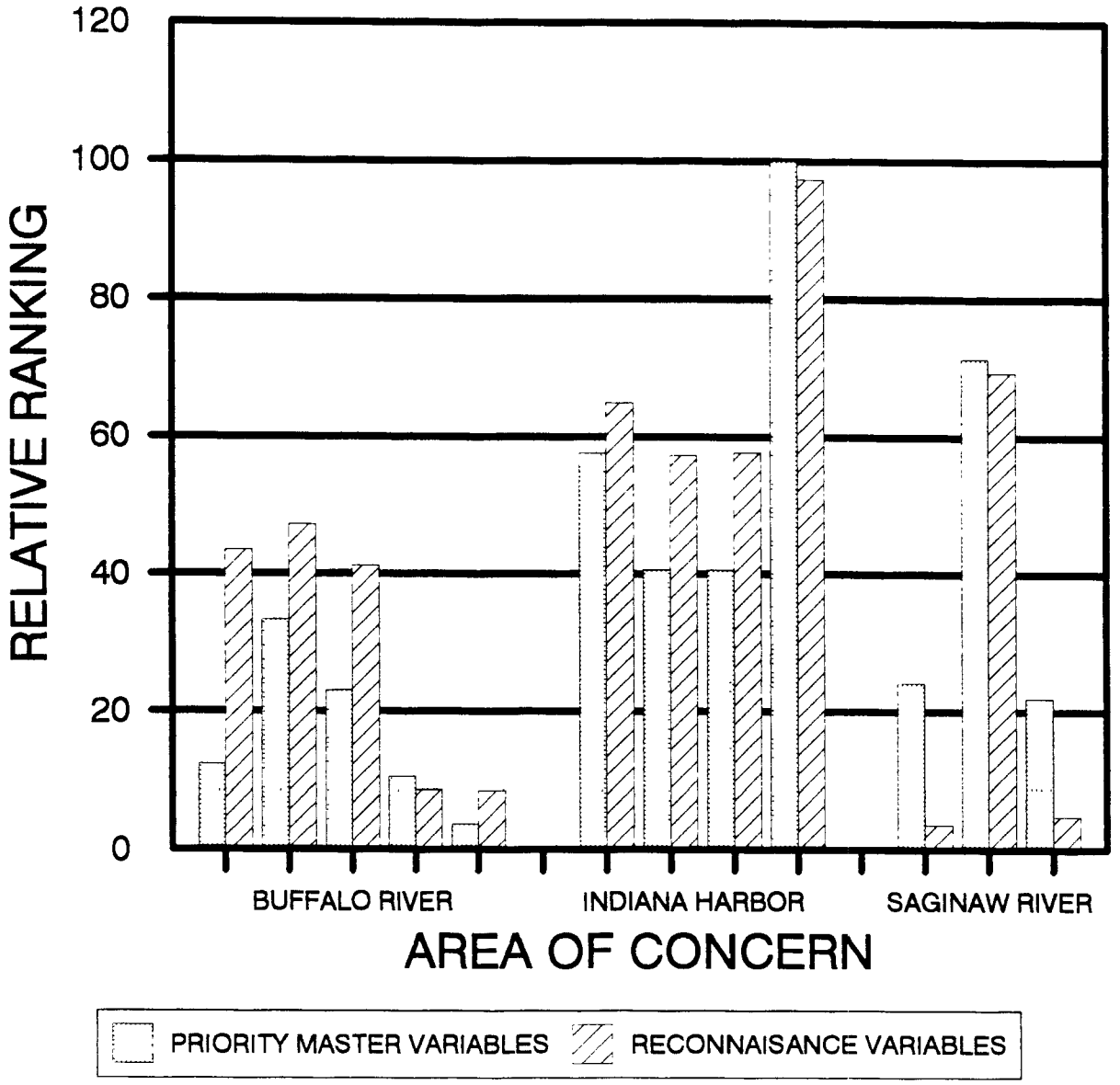

Figure 11. Comparison of the overall ranking of sites based on Priority Master Stations (shaded bars) versus Reconnaissance Stations (crosshatched bars). Bars represent the average of the relative ranking among sites of toxic units, control-adjusted laboratory toxicity, and mean tolerance to pollution of the benthic community for Priority Master Stations. For Reconnaissance Stations, bars represent the average of the relative ranking among sites of toxic units, which were base only a short list of contaminants, and Microtox.

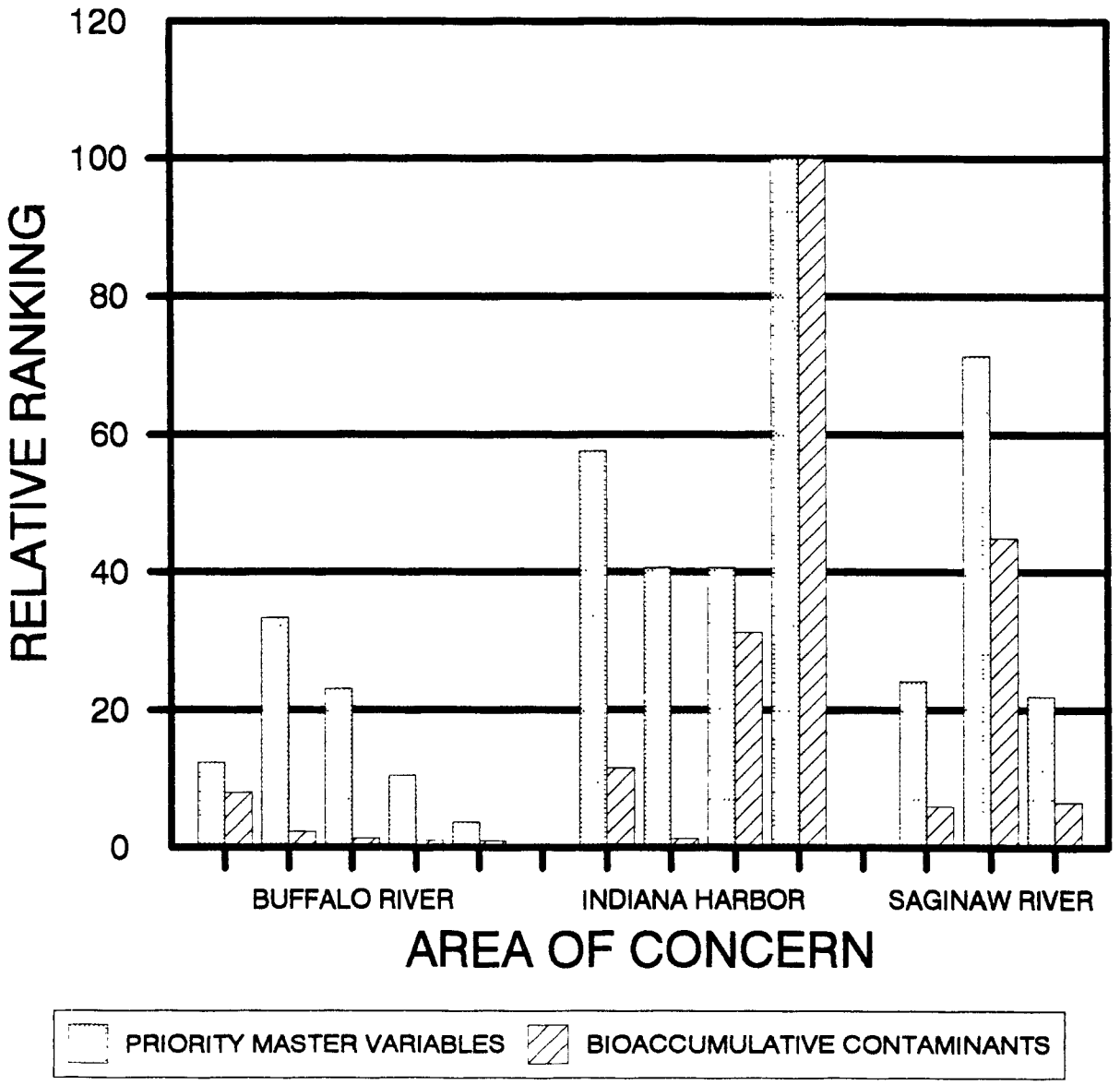

Figure 12. Comparison of the overall ranking of sites based on Priority Master Stations (shaded bars) versus bioaccumulative contaminants (crosshatched bars). Bars represent the average of the relative ranking among sites of toxic units, control-adjusted laboratory toxicity, and mean tolerance to pollution of the benthic community for Priority Master Stations. For bioaccumulative contaminants, bars represent the toxic units based on bulk concentrations of those contaminants listed as bioaccumulative contaminants of concern (Table 5).